Metcalfe and Yarborough (*15*) data which indicated that the interaction coefficients of the SRK equation of state mixing rules are functions of pressure. Therefore, it would be highly conjectural to make calculations of maximum miscibility composition at other pressure levels with any of the interaction coefficient sets of Table III.

Our data and those of Metcalfe and Yarborough (*15*) should be analyzed in terms of other equations of state which might better predict carbon dioxide-hydrocarbon phase behavior. More multicomponent carbon dioxide-hydrocarbon data should be acquired at other pressures and temperatures to further test equations of state being employed for phase equilibria calculations.

Glossary

k	SRK interaction coefficient, dimensionless
p	pressure, kPa
x	mole fraction, dimensionless

Suffixes

1	carbon dioxide
2	*n*-butane
3	*n*-decane
4	*n*-butylcyclohexane
5	*n*-butylbenzene

Registry No. *n*-Butane, 106-97-8; *n*-decane, 124-18-5; *n*-butylcyclohexane, 1678-93-9; *n*-butylbenzene, 104-51-8; carbon dioxide, 124-38-9.

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Adsorption of Oxygen, Nitrogen, and Argon on 5A Molecular Sieve

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A static experimental setup is described for the measurement of multicomponent adsorption equilibria. Single-component and binary isotherms on 5A molecular sieve are obtained for oxygen, nitrogen, and argon at temperatures between 0 and 75 °C and pressures ranging from 0 to 5 bar. Literature data in this range are scarce, often inaccurate, but are vital to the study of pressure swing adsorption for separation of air. Careful calibration and automation allowed us to obtain accuracies of 0.1% on pressures (electronic transducers) and 0.2% on concentrations (quadrupole mass spectrometer). The data can be fitted equally well with a multicomponent Langmuir isotherm and a model isotherm of Ruthven over this practical temperature and pressure range.

Introduction

Accurate multicomponent adsorption equilibrium data are important for use in the design and simulation of pressure swing adsorption apparatus for separation of gas or vapor mixtures (*1*). A number of these adsorption units are operated at temperatures above 0 °C and pressures of a few bar. The literature contains little information for those operating conditions. A good example is the industrially important air separation on 5A molecular sieve. Very few single-component and multicomponent data or correlations are available in this range for adsorption of oxygen, nitrogen, and argon mixtures on 5A molecular sieve (*2-6*). Only one set of data on O_2-N_2 mixtures is fairly complete but unfortunately does not agree with other literature data and our own data on the amount adsorbed (differences of about 20%). A new and accurate data set over a wide range of pressures and temperatures seems thus useful.

Since diffusion and the resulting mixing are rapid at these elevated temperatures, there is no need to use a mixing device to obtain a uniform composition in the adsorption apparatus. A static method can be used with measurement of pressures before and after introducing a known amount of gas mixture in an adsorption cell and a single measurement of the resulting gas-phase concentration. In this way, a number of technical problems encountered with recirculation methods (*7*) or chromatographic methods (*3*) are avoided. The measurement of gas-phase concentration has to be performed without disturbing the equilibrium, so only a small sample can be withdrawn, which is no problem with mass spectrometry.

Apparatus and Experimental Procedure

The experimental setup is described below with reference to Figure 1. It consists essentially of two stainless steel pressure vessels with temperature, pressure, and concentration measurements, and a number of connecting lines and valves. All lines are $^1/_8$-in. o.d. and all valves $^1/_8$-in. ball valves (Whitey, Swagelok) except valves 2, 6, 7, which are 1/16-in. miniature regulating and shut-off valves (Nupro) and their connecting lines (1/16-in. o.d., 0.25-mm i.d.), so as to minimize their holdup. Each pressure vessel is equipped with a PT100 temperature sensor (0.1 °C accuracy) and an electronic pressure transducer (Druck Ltd. U.K., PDCR 10, 0.1% accuracy).

The adsorption cell is partially filled with an accurately weighed sample of freshly regenerated adsorbent through a fill opening closed with a plug. It is placed in a thermostatic bath,

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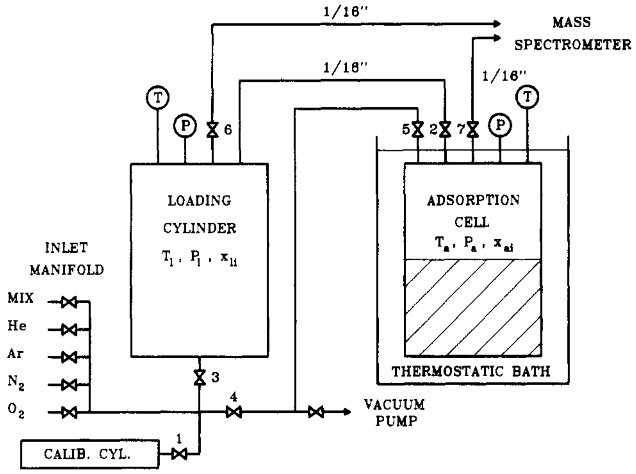

Figure 1. Schematic drawing of the experimental apparatus.

such that the valves and the pressure transducer are at the same temperature, controlled to within 0.1 °C. The adsorption cell (±300 mL), the loading cylinder (±500 mL), and the inlet manifold can be evacuated by opening valves 5, 3, and 4. The gas-phase concentration can be measured by opening the valves 6 or 7 to the mass spectrometer inlet capillary. A fully computer-controlled quadrupole mass spectrometer (Balzers QMG 511) was used.

Careful calibration with gas mixtures over the entire range of concentration allowed for 0.2% accuracy. An analysis can be performed without disturbing the contents of the two vessels since only a small quantity (0.1 mL typically) is needed. The free gas volumes in the two vessels, fitted with their connections and instruments, are determined by differential pressurization measurements with the gas from a third calibration vessel with accurately known volume.

A typical experiment then runs as follows. The whole system is evacuated by opening valves 3–5. All valves are then closed. A pure component or a mixture is then introduced in the loading cylinder from the inlet manifold through valve 3 until a certain pressure is read. Then valve 3 is closed again. Sufficient time is waited to obtain stable pressure and temperature readings. Valve 2 is then opened for a short period such that an adequate amount of the mixture flows to the adsorption cell, after which valve 2 is closed again. Equilibrium between gas and solid is fairly rapidly reached, but thermal equilibrium has to be awaited since temperature has a strong influence on the amount adsorbed. The time one has to wait depends on temperature and pressure levels and ranges from 10 to 60 min in extreme cases. This is no problem since the equipment can easily be made perfectly leaktight. Now samples are withdrawn and analyzed by opening valve 7 and, if necessary, valve 6 to the mass spectrometer.

The equilibrium data are easily extracted from these primary pressure, temperature, and concentration measurements by solving the mass balances for the N components i over both vessels, before (0) and after (1) adsorption:

$$\left.\frac{x_{il}P_lV_l}{Z_lRT_l}\right|_0 = \left.\frac{x_{il}P_lV_l}{Z_lRT_l}\right|_1 + \frac{x_iP_aV_a}{Z_aRT_a} + Mny_i \qquad (1)$$

$$i = 1, ..., N$$

with

$$\sum_{i=1}^{N} y_i = 1 \qquad (2)$$

for the $N + 1$ unknowns n (total amount adsorbed) and y_i (mole fractions on adsorbent). In the conditions of relatively high temperatures and low pressures we worked in, the compressibilities in eq 1 can be taken to be unity within experimental error.

Table I. Nitrogen Adsorption on Molecular Sieve 5A

T, K	P, bar	n, mol/kg	T, K	P, bar	n, mol/kg
273.55	0.385	0.278	319.85	0.737	0.145
273.55	0.815	0.507	319.85	1.003	0.195
273.55	1.161	0.653	319.85	1.519	0.279
273.55	1.445	0.752	319.85	1.976	0.350
273.55	1.917	0.903	319.85	2.135	0.376
273.55	2.611	1.076	319.85	2.481	0.421
273.55	3.457	1.235	319.85	2.983	0.487
273.55	3.927	1.310	319.85	3.668	0.573
298.55	0.341	0.124	319.85	4.234	0.636
298.55	0.726	0.241	347.95	0.323	0.360
298.55	1.025	0.327	347.95	0.720	0.0791
298.55	1.491	0.441	347.95	1.019	0.1115
298.55	1.954	0.544	347.95	1.281	0.1394
298.55	2.741	0.698	347.95	1.532	0.1649
298.55	3.170	0.760	347.95	2.028	0.2129
298.55	3.633	0.829	347.95	2.549	0.2593
298.55	4.024	0.881	347.95	2.985	0.2986
298.55	4.429	0.933	347.95	3.505	0.3422
319.55	0.359	0.071	347.95	3.990	0.3823
319.85	0.520	0.107			

Table II. Oxygen Adsorption on Molecular Sieve 5A

T, K	P, bar	n, mol/kg	T, K	P, bar	n, mol/kg
273.55	0.374	0.072	319.85	0.365	0.026
273.55	0.716	0.135	319.85	0.780	0.059
273.55	1.000	0.186	319.85	1.161	0.089
273.55	1.475	0.270	319.85	1.593	0.121
273.55	1.987	0.357	319.85	2.055	0.155
273.55	2.432	0.429	319.85	3.086	0.227
273.55	2.990	0.510	319.85	3.550	0.256
273.55	3.460	0.582	319.85	4.046	0.291
273.55	3.928	0.650	347.95	0.336	0.0174
298.55	0.293	0.034	347.95	0.737	0.0387
298.55	0.689	0.078	347.95	1.045	0.0546
298.55	1.106	0.125	347.95	1.502	0.0777
298.55	1.552	0.174	347.95	2.004	0.1033
298.55	2.027	0.223	347.95	2.604	0.1330
298.55	2.499	0.271	347.95	3.010	0.1529
298.55	2.962	0.314	347.95	3.514	0.1755
298.55	3.537	0.367	347.95	4.007	0.1992
298.55	4.048	0.413			

This equipment was used to determine the adsorption equilibria of N_2, O_2, and Ar mixtures on 5A molecular sieve. Nitrogen and argon used in this study were better than 99.9 mol % pure and oxygen 99.7% pure with 0.3% argon. The adsorbent was 5A Silliporite NK20 (Ceca—France) with about 20% by weight of inert clay binder. The sieve (2-mm beads) was ground and sieved to obtain a fraction between 250 and 425 μm for our adsorption experiments. A sample of this was used to obtain the present data. Comparison with the original sieve showed that the relative amount of clay binder in the obtained fraction had increased to 28%. Otherwise its properties were unchanged. Prior to a set of experiments, the sieve was conditioned by heating in air to 260 °C for 48 h and then always kept under slight overpressure with dry air or nitrogen. In this way we avoided hysteresis effects encountered when regenerating at higher temperatures and under vacuum as described in ref 4.

Results

The experimental results for the pure components N_2, O_2, and Ar are given in Tables I–III. As the data should serve in the design of PSA systems for O_2 production, operating at a few bar and around ambient temperature, only the binary N_2–O_2 was determined. The low concentrations of Ar and its similarity to O_2 in adsorption behavior (see further) did not justify

Table III. Argon Adsorption on Molecular Sieve 5A

T, K	P, bar	n, mol/kg	T, K	P, bar	n, mol/kg
273.55	0.315	0.049	319.85	0.345	0.0248
273.55	0.694	0.113	319.85	0.798	0.0570
273.55	1.040	0.168	319.85	1.079	0.0771
273.55	1.500	0.241	319.85	1.574	0.1116
273.55	1.974	0.316	319.85	2.033	0.1436
273.55	2.501	0.391	319.85	2.772	0.1928
273.55	2.974	0.458	319.85	3.102	0.2140
273.55	3.536	0.538	319.85	3.553	0.2420
273.55	3.989	0.592	319.85	4.019	0.2722
298.55	0.355	0.0378	347.95	0.348	0.0144
298.55	0.793	0.0819	347.95	0.729	0.0332
298.55	1.090	0.1119	347.95	1.038	0.0480
298.55	1.575	0.1596	347.95	1.524	0.0714
298.55	2.050	0.2053	347.95	1.998	0.0919
298.55	2.540	0.2517	347.95	2.011	0.0938
298.55	3.008	0.2951	347.95	2.522	0.1177
298.55	3.561	0.3419	347.95	3.091	0.1419
298.55	4.136	0.3925	347.95	3.514	0.1614
298.55	4.387	0.4145	347.95	4.012	0.1827

Table IV. Adsorption of Nitrogen (1)-Oxygen (2) Mixtures on 5A Molecular Sieve

T, K	P, bar	x_1	y_1	Δy_1	n	Δn
298.55	1.040	0.632	0.847	0.003	0.262	0.007
298.55	1.040	0.635	0.847	0.001	0.263	0.007
298.55	1.040	0.347	0.621	-0.004	0.199	0.003
298.55	1.040	0.100	0.260	0.000	0.142	0.000
298.55	1.040	0.811	0.928	-0.003	0.298	0.007
298.55	1.040	0.787	0.915	-0.006	0.294	0.007
298.55	1.040	0.462	0.724	-0.005	0.223	0.002
298.55	1.040	0.225	0.472	-0.005	0.173	0.003
298.55	1.040	0.223	0.474	-0.002	0.174	0.005
298.55	3.000	0.657	0.848	-0.009	0.622	0.001
298.55	3.000	0.229	0.478	-0.005	0.439	0.001
298.55	3.000	0.099	0.254	-0.004	0.376	0.004
298.55	3.000	0.353	0.628	-0.003	0.501	0.005
298.55	4.000	0.664	0.850	-0.011	0.761	-0.002
298.55	4.000	0.100	0.257	-0.002	0.478	0.002
319.85	1.040	0.115	0.260	0.004	0.096	-0.001
319.85	1.040	0.678	0.851	0.004	0.167	0.002
319.85	1.040	0.263	0.492	0.006	0.117	0.002
319.85	1.040	0.391	0.631	0.001	0.133	0.002

an extensive study of the binaries O_2-Ar and N_2-Ar. A few experiments showed that for conditions encountered in industrial practice Ar and O_2 can be pooled and the data of O_2 can be used without loss of accuracy. Table IV gives a number of binary data at various temperatures and pressures.

Many isotherms could be used to fit these data (*6*), especially the model isotherm of Ruthven (*2*) which has a theoretical foundation. For practical use in design a simple closed form like the Langmuir isotherm appears to fit our data quite well, almost within experimental error, although there is no theoretical basis whatsoever in the case of molecular sieves.

The multicomponent Langmuir isotherm can be written as (N components)

$$n_i = y_i n = K_i x_i P / (1 + \sum_{i=1}^{N} L_i x_i P) \tag{3}$$

with

$$n = \sum_{i=1}^{N} n_i \tag{4}$$

$$K_i = K_{i0} \exp(q_i/RT) \tag{5}$$

$$L_i = L_{i0} \exp(q_i/RT) \tag{6}$$

Single-component isotherms were fitted and K_i and L_i determined at the four temperatures by nonlinear least-squares fit (*8*). An example of good correlation is shown in Figure 2. The average fitting error is 0.2%, which is the estimated experimental error. This is much lower than for the data available in the literature. The obtained values of K_i and L_i are given in Tables V and VI. Then the K_{i0} and q_i values were determined by a fit of the K_i values to eq 5. Figure 3 shows the excellent agreement with the Arrhenius equation (5).

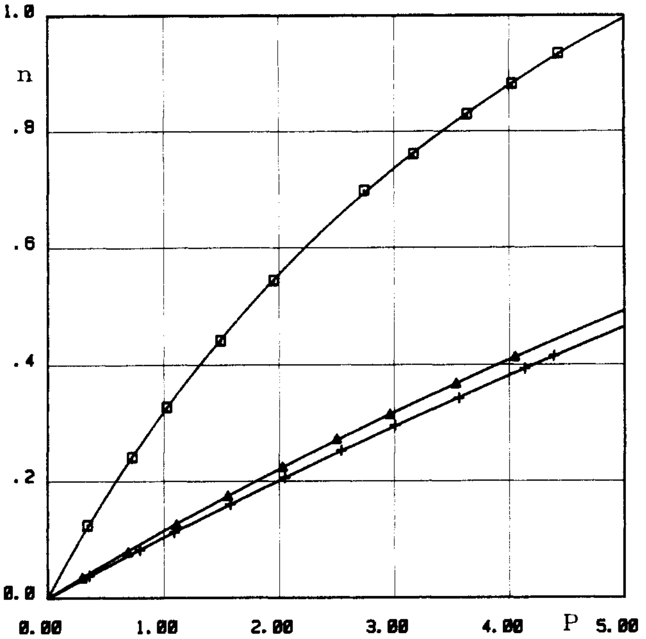

Figure 2. Adsorption isotherms for N_2 (□), O_2 (△), and Ar (+) at 298.55 K on 5A molecular sieve.

Table V. Constant K_i (mol/(kg•bar)) for N_2, O_2, and Ar Adorption on 5A Molecular Sieve in the Langmuir Equation (3)

	K_i		
T, K	N_2	O_2	Ar
273.55	0.7798	0.1953	0.1718
298.55	0.3755	0.1196	0.1060
319.85	0.2098	0.0786	0.0736
347.95	0.1156	0.0537	0.0476

Table VI. Constant L_i (bar^{-1}) for N_2, O_2, and Ar Adsorption on 5A Molecular Sieve in the Langmuir Equation (3)

	L_i		
T, K	N_2	O_2	Ar
273.55	0.3414	0.0465	0.0385
298.55	0.1773	0.0430	0.0280
319.85	0.0940	0.0236	0.0218
347.95	0.0516	0.0200	0.0110

Table VII. Parameters in Eq 5 and 6 for the Multicomponent Langmuir Isotherm (Eq 3) for N_2, O_2, and Ar on 5A Molecular Sieve

component	$\ln K_{i0}$	$\ln L_{i0}$	q_i, kJ/mol
N_2	-9.222	-10.018	20.42
O_2	-7.745	-8.908	13.91
Ar	-7.730	-9.108	13.59

At the studied low pressures, far from saturation, the curvature of the isotherms is weak and the denominator part in eq 3 is close to unity. The L_i values are small and plotting them in an Arrhenius diagram (Figure 4) reveals the uncertainty in the data, especially for the O_2 and Ar isotherms with weakest curvature. As q_i has already been determined with high accuracy from the K_i, it is sufficient to find the L_{i0} in eq 6. The corresponding fitted lines are plotted in Figure 4 and still give a reasonable agreement, considering the small magnitude of the denominator terms. Anyhow, these terms also contribute

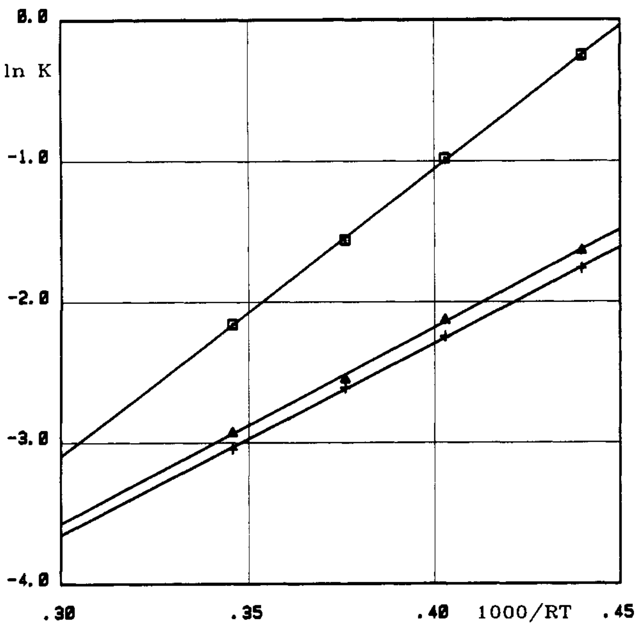

Figure 3. Arrhenius diagram for the Henry constant for N_2 (□), O_2 (△), and Ar (+).

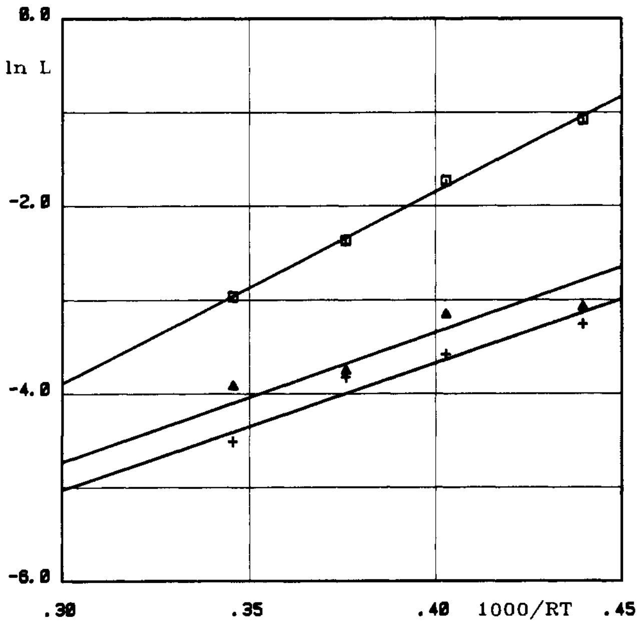

Figure 4. Arrhenius diagram for the Langmuir constants for N_2 (□), O_2 (△), and Ar (+).

very little to the value predicted by eq 3.

Table VII gives the obtained K_{i0}, L_{i0}, and q_i values for the three components. The isosteric heats of adsorption are well in the range of available literature data. Values of 21 kJ/mol for N_2 (*3*, *4*) and 14 kJ/mol for O_2 (*3*) are reported. Note the similar behavior of O_2 and Ar.

Recomputing the experimental values of Tables I-III with the global equations 3-6 and the values of Table VII yielded average deviations of 0.4% in the amount adsorbed. This is quite good considering the range over which these equations are used.

The experimental binary data of Table IV were compared to the predictions by eq 3-6 and the parameters of Table VII. The deviations on total amount adsorbed (Δn) and adsorbed N_2 mole fraction (Δy) are given in Table IV. An average error of 0.4% on mole fractions and of 0.4% on the adsorbed amount is found (Figures 5 and 6). The errors are thus of the order of those found with the pure components. The pure-component parameters appear to yield an accurate prediction of the binary mixture equilibria, at least in the studied range of temperatures and pressures. Again, the spread in the data of Table IV is much smaller than in those reported in the literature.

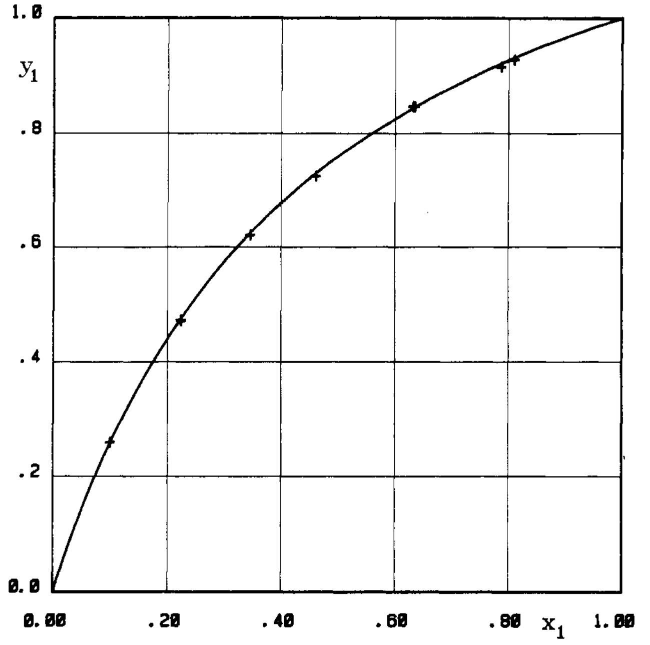

Figure 5. Equilibrium curve for the binary O_2–N_2 at 1.04 bar and 298.55 K: experimental (+) and predicted values (—).

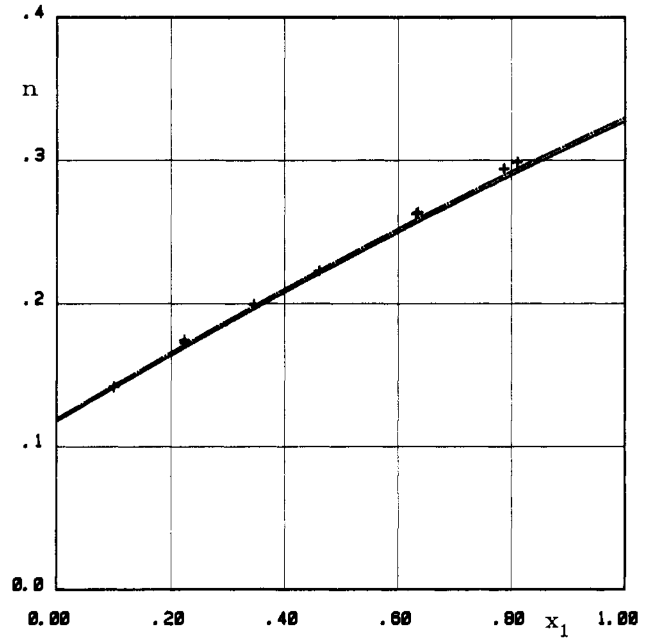

Figure 6. Total amount absorbed at 1.04 bar and 298.55 K for the binary O_2–N_2. Experimental (+) and predicted values: (—) global fit, (---) K_i, L_i at 298.55 K.

A somewhat better prediction is obtained for the amount adsorbed when the values of K_i and L_i at 298.55 K are taken instead of those computed from eq 5 and 6 (Figure 6). As the residual errors correspond to temperature differences of 0.3 °C, there does not seem much room for further improvement.

Fitting the Ruthven isotherm (*2*) to our data did not yield any better fit, or prediction of the binary data. The Ruthven isotherm would only be useful at higher pressures or lower temperatures. The obtained parameters agree well with those reported in the literature. The pressure range was however too limited (especially for O_2 and Ar) to determine them with high accuracy at these temperatures.

Glossary

K	constant in eq 3, mol/(kg·bar)
L	constant in eq 3, bar^{-1}
M	mass of adsorbent, kg
n	amount absorbed, mol/kg
P	pressure, bar
q	isosteric heat of adsorption, kJ/mol
R	gas law constant
T	temperature, K
V	gas-phase volume, m^3
x_i	gas-phase mole fraction
y_i	adsorbent-phase mole fraction
Z	compressibility factor

Subscripts

i	component number
I	in loading cylinder
a	in adsorption cell

Registry No. O_2, 7782-44-7; N_2, 7727-37-9; Ar, 7440-37-1.

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Solubility of Phenylacetic Acid in Binary Solvent Mixtures

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Solubilities are reported for phenylacetic acid at 25.0 °C in binary mixtures of carbon tetrachloride with cyclohexane, *n*-heptane, *n*-octane, or isooctane and mixtures of cyclohexane with *n*-heptane or isooctane. The results are compared to the predictions of equations developed previously for solubility in systems of purely nonspecific interactions, with phenylacetic acid considered as either monomeric or dimeric molecules in solution. The dimer model provided the more accurate predictions and described the 15-fold range of solubilities in the carbon tetrachloride + isooctane system to within a maximum deviation of 15%.

Introduction

This work continues a systematic search (*1–8*) for mixing models and equations which will provide reasonable predictions for the thermochemical properties of a solute in binary solvent mixtures. In an earlier paper, Acree and Bertrand (*3*) reported benzoic acid and *m*-toluic acid solubilities in solvent mixtures containing carbon tetrachloride. The experimental data were interpreted with solution models based on a monomeric treatment

$$RT \ln (a_{3,\mathrm{mon}}^{\mathrm{solid}}/X_{3,\mathrm{mon}}^{\mathrm{sat}}) = (1 - \phi_{3,\mathrm{mon}}^{\mathrm{sat}})^2[\phi_1{}^\circ(\Delta\bar{G}_{3,\mathrm{mon}}^{\mathrm{ex}})^*{}_{X_1{}^\circ=1} + \phi_2{}^\circ(\Delta\bar{G}_{3,\mathrm{mon}}^{\mathrm{ex}})^*{}_{X_2{}^\circ=1} - \bar{V}_{3,\mathrm{mon}}(X_1{}^\circ\bar{V}_1 + X_2{}^\circ\bar{V}_2)^{-1}(\Delta\bar{G}_{12}^{\mathrm{ex}})] \quad (1)$$

$$RT[\ln (a_{3,\mathrm{mon}}^{\mathrm{solid}}/\phi_{3,\mathrm{mon}}^{\mathrm{sat}}) - (1 - \phi_{3,\mathrm{mon}}^{\mathrm{sat}})(1 - \bar{V}_{3,\mathrm{mon}}/(X_1{}^\circ\bar{V}_1 + X_2{}^\circ\bar{V}_2))] = (1 - \phi_{3,\mathrm{mon}}^{\mathrm{sat}})^2[\phi_1{}^\circ(\Delta\bar{G}_{3,\mathrm{mon}}^{\mathrm{fh}})^*{}_{X_1{}^\circ=1} + \phi_2{}^\circ(\Delta\bar{G}_{3,\mathrm{mon}}^{\mathrm{fh}})^*{}_{X_2{}^\circ=1} - \bar{V}_{3,\mathrm{mon}}(X_1{}^\circ\bar{V}_1 + X_2{}^\circ\bar{V}_2)^{-1}(\Delta\bar{G}_{12}^{\mathrm{fh}})] \quad (2)$$

and a dimeric treatment

$$RT \ln (a_{3,\mathrm{dim}}^{\mathrm{solid}}/X_{3,\mathrm{dim}}^{\mathrm{sat}}) = (1 - \phi_{3,\mathrm{dim}}^{\mathrm{sat}})^2[\phi_1{}^\circ(\Delta\bar{G}_{3,\mathrm{dim}}^{\mathrm{ex}})^*{}_{X_1{}^\circ=1} + \phi_2{}^\circ(\Delta\bar{G}_{3,\mathrm{dim}}^{\mathrm{ex}})^*{}_{X_2{}^\circ=1} - \bar{V}_{3,\mathrm{dim}}(X_1{}^\circ\bar{V}_1 + X_2{}^\circ\bar{V}_2)^{-1}(\Delta\bar{G}_{12}^{\mathrm{ex}})] \quad (3)$$

$$RT[\ln (a_{3,\mathrm{dim}}^{\mathrm{solid}}/\phi_{3,\mathrm{dim}}^{\mathrm{sat}}) - (1 - \phi_{3,\mathrm{dim}}^{\mathrm{sat}})(1 - \bar{V}_{3,\mathrm{dim}}/(X_1{}^\circ\bar{V}_1 + X_2{}^\circ\bar{V}_2))] = (1 - \phi_{3,\mathrm{dim}}^{\mathrm{sat}})^2[\phi_1{}^\circ(\Delta\bar{G}_{3,\mathrm{dim}}^{\mathrm{fh}})^*{}_{X_1{}^\circ=1} + \phi_2{}^\circ(\Delta\bar{G}_{3,\mathrm{dim}}^{\mathrm{fh}})^*{}_{X_2{}^\circ=1} - \bar{V}_{3,\mathrm{dim}}(X_1{}^\circ\bar{V}_1 + X_2{}^\circ\bar{V}_2)^{-1}(\Delta\bar{G}_{12}^{\mathrm{fh}})] \quad (4)$$

of the carboxylic acid. Deviations between observed and predicted values were on the order of 6–10% for eq 1 (and eq 2) and 2–4% for eq 3 (and eq 4).

While this earlier study did suggest that a dimeric treatment is more applicable for describing the properties of benzoic acid and *m*-toluic acid, the model should be tested by using several carboxylic acid solutes. For this reason, I have measured the solubility of phenylacetic acid in several binary solvent systems containing carbon tetrachloride with cyclohexane, *n*-heptane, *n*-octane, and isooctane and mixtures of cyclohexane with *n*-heptane and isooctane. These systems will provide a more demanding test for eq 3 and 4 as phenylacetic acid is 13 times more soluble (on a mole fraction basis) in carbon tetrachloride than in the *n*-alkane solvents.

Experimental Section

Phenylacetic acid (98.5%) was recrystallized several times from cyclohexane, mp 76.5 ± 0.5 °C [lit. (*9*) mp 77 °C]. The recrystallized acid was titrated to a thymol blue end point with freshly standardized sodium methoxide by the method of Fritz and Lisicki (*10*), except toluene was substituted for benzene. The purity of the phenylacetic acid was calculated to be 99.7 ± 0.5%. Cyclohexane (99+%), *n*-heptane (99+%), *n*-octane (99+%), and isooctane (99+%) were stored over molecular sieves (type 4A) and distilled shortly before use. Carbon tetrachloride (99%) was purified by the method of Scatchard et al. (*11*), stored in contact with mercury under an argon atmosphere, and distilled shortly before use.

Solvent mixtures were prepared by weight with sufficient accuracy to allow calculation of compositions to 0.0001 mole fraction. Solvents and excess carboxylic acid were placed in amber glass containers and allowed to equilibrate in a constant-temperature shaker bath at 25.0 ± 0.1 °C for several days. Attainment of equilibrium was verified by repetitive measurements after several additional days. Acid solubilities were determined by transferring weight aliquots through a coarse filter into flasks containing blank nonaqueous titration solvent. The solutions were titrated with freshly standardized

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