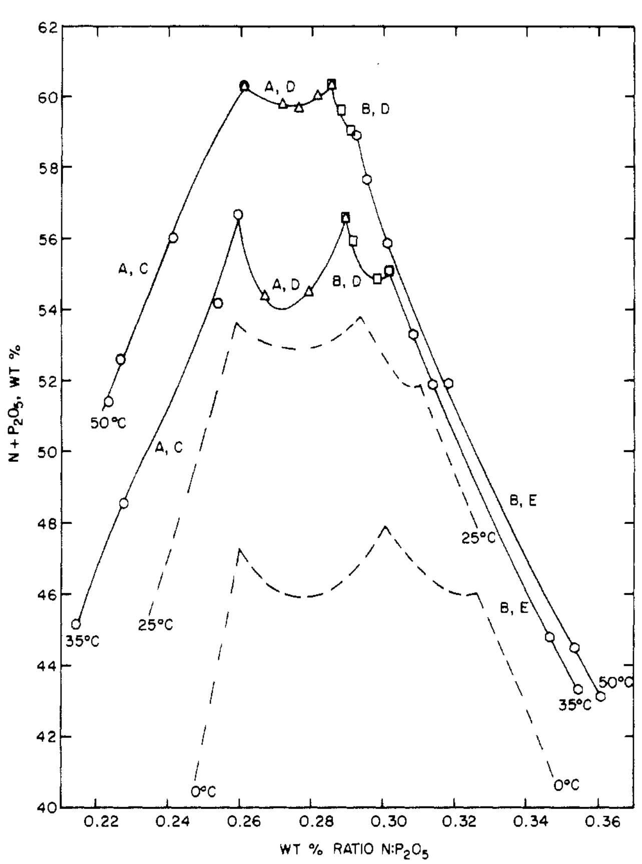

Figure 1. Solubility in ammonium ortho- and pyrophosphate systems at 35 and 50 °C [saturating solids: A = $NH_4H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_2H_2P_2O_7$, D = $(NH_4)_3HP_2O_7 \cdot H_2O$, E = $(NH_4)_4P_2O_7$].

comprise four branches representing the salt pairs $NH_4H_2PO_4$ and $(NH_4)_2H_2P_2O_7$, $NH_4H_2PO_4$ and $(NH_4)_3HP_2O_7 \cdot H_2O$, $(NH_4)_2HPO_4$ and $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_2HPO_4$ and $(NH_4)_4P_2O_7$.

The composition of three invariant solutions was determined at both temperatures. The three salts found at the three invariant points were $NH_4H_2PO_4$, $(NH_4)_2H_2P_2O_7$, and $(NH_4)_3HP_2O_7 \cdot H_2O$; $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_3HP_2O_7 \cdot H_2O$; and $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_4P_2O_7$. The most concentrated solutions ($N + P_2O_5$) are found in the region adjacent to the two invariant points with the lowest pH. In those two invariant points with the highest pH, there is a pronounced decrease in the ratio $N:P_2O_5$ as the temperature increases. In the invariant solutions with the lowest pH, the ratio $N:P_2O_5$ remains essentially constant over the temperature range 0-50 °C.

Registry No. NH_3, 7664-41-7; H_3PO_4, 7664-38-2; $H_4P_2O_7$, 2466-09-3.

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Adsorption of Ethylene/Ethane Mixtures on a Carbon Molecular Sieve

Tomoko Nakahara* and Toshio Wakai

Department of Industrial Chemistry, Faculty of Technology, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan

Adsorption equilibria for the system of ethylene-ethane-carbon molecular sieve (MSC·5A) were measured at temperatures (and pressures) of 10 °C (0.67, 2.67, 4.00, 6.67, 13.33, and 20.00 kPa), 20 °C (0.67, 2.00, 5.33, and 10.67 kPa), and 40 °C (0.67, 3.33, 9.33, and 22.66 kPa). The adsorption isotherms of pure ethylene and ethane were determined at 10, 20, 30, and 40 °C at pressures of 1.5-47 kPa. Henry's law was not applicable to the adsorption in the low-pressure region because of the existence of high-energy sites from which the adsorbed molecules cannot be removed reversibly in the micropores.

Introduction

Adsorption equilibrium data for multicomponent gaseous mixtures are essential for designing adsorption plants, and the data are also of interest for the thermodynamics of adsorption. The solid adsorbents often have heterogeneous surfaces and are rich in micropores. Although the actual separation of gases are made at comparatively high pressures, the thermodynamical interest for the prediction calculation from the pure isotherms exists in the adsorption at low pressures where the heterogeneity and the characteristics of micropores appear significantly. In this study we measured the adsorption equilibrium data for binary gaseous mixtures of ethylene and ethane on a carbon molecular sieve (MSC·5A) at temperatures (and pressures) of 10 °C (0.67, 2.67, 4.00, 6.67, 13.33, and 20.00 kPa), 20 °C (0.67, 2.00, 5.33, and 10.67 Pa), and 40 °C (0.67, 3.33, 9.33, and 22.66 kPa). The adsorption isotherms of the pure components also were determined at 10, 20, 30, and 40 °C and at pressures from 1.5 to 47 000 Pa. The adsorption equilibrium data at 30 °C for this binary gaseous system were previously reported (*1*).

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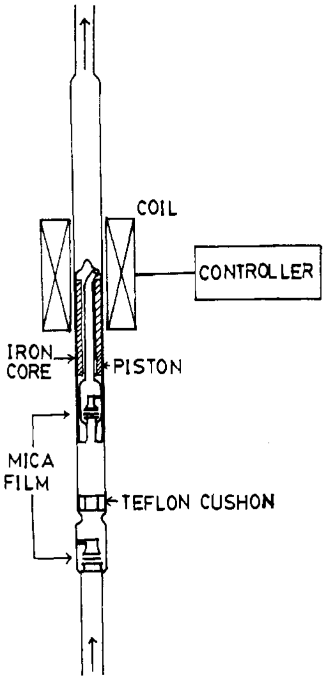

Figure 1. Piston pump made of glass.

Experimental Section

The carbon molecular sieve (MSC-5A) used in this work has the same physical properties as that used in the previous works (*1*, *2*). The purities of ethylene and ethane were both 99.7 mol %. The adsorption isotherms of pure components were determined with an electric balance (Cahn RG-HV); the pressures were determined with a Digiquartz Pressure Transducer (Paroscientific Inc.) for the measurements at 1.5–4.7 kPa and Baratron 221A for the measurements at 1.5–1333 Pa. The experimental points were obtained in the desorption process by reducing the pressure little by little after the adsorbent had been equilibrated with the adsorbate for 24 h at 4.7 kPa. The reason for taking the desorption process was that at the very first stage of adsorption it took about 24 h for the gas to diffuse into the very narrow micropores of adsorbent, and because it was difficult to accurately maintain at a pressure as low as 1.5 Pa for 24 h. The time for attaining the equilibrium, when the sites of high energies had been occupied, was about 20 min.

A very small amount of adsorbate was not removed from the adsorbent after evacuation at 0.0015 Pa for 20 h at equilibrium temperature. This remaining adsorbate could be removed by heating at 360 °C at 0.0015 Pa. The difference in the kinetic energy of polyatomic molecules at 10 °C and at 360 °C is $3R\Delta T$ = 2.2 kcal/mol (*3*). This means that the molecules adsorbed at the sites of high energies, which generally exist in the very narrow micropores, require about 2.2 kcal/mol to move to the sites from which the molecules are reversibly desorbable.

The apparatus used for the measurements of adsorption equilibria for the system of ethylene–ethane–MSC-5A was essentially the same as the one previously reported (*1*), excepting that the glass piston pump (Figure 1) was attached to the adsorption column in order to attain faster homogenization of the gas phase. The pump circulated the gas by absorbing it from the inlet which was situated at the bottom and by discharging it through the outlet at the top of the column. The pump worked at pressures of 15–10^5 Pa, and its airflow volume was 1.3–4.0 L/min; the maximum pressure difference was 2 × 10^4 Pa. The iron core in the pump was sealed in glass in order to make the pump corrosion-resistant. The inside volume of the pump was 5 mL and the surface area which may adsorb the sample gas

Table I. Coefficients and Errors of Polynomial Equation for Pure Isotherms[a]

	ethylene				ethane			
C_i	10 °C	20 °C	30 °C	40 °C	10 °C	20 °C	30 °C	40 °C
i =								
0	−0.16076210E+01	−0.18107330E+01	−0.21054660E+01	−0.17740424E+01	−0.11697185E+01	−0.14374713E+01	−0.18811166E+01	−0.15145839E+01
1	0.15953633E+01	0.17974937E+01	0.25422699E+01	0.14467494E+01	0.28090262E−01	0.10571536E+01	0.23556059E+01	0.58609520E+00
2	−0.268822121+01	−0.29279930E+01	−0.36689522E+01	−0.23107298E+01	−0.19531976E+00	−0.16853140E+01	−0.36230355E+01	−0.10439271E+01
3	0.24307187E+01	0.24575802E+01	0.27086321E+01	0.18005332E+01	0.53147744E+00	0.14955721E+01	0.29126693E+01	0.91002966E+00
4	−0.10974044E+01	−0.10273034E+01	−0.10256183E+01	−0.69370930E+00	−0.30585118E+00	−0.63795705E+00	−0.12106877E+01	−0.33386808E+00
5	0.26730831E+00	0.23215065E+00	0.21262242E+00	0.14683855E+00	0.81437535E−01	0.14509032E+00	0.27658944E+00	0.61050698E−01
6	−0.33803040E−01	−0.27352247E−01	−0.23139874E−01	−0.16553610E−01	−0.10740069E−01	−0.17137069E−01	−0.33210291E−01	−0.54581591E−02
7	0.17433519E−02	0.13212409E−02	0.10371350E−02	0.77992625E−03	0.56833511E−03	0.82967015E−03	0.16415646E−02	0.18434435E−03
std dev, mmol/g of adsorbent	0.0248	0.00579	0.00197	0.00689	0.00564	0.00109	0.00845	0.0119
unremovable adsorpn, mmol/g of adsorbent	0.0728	0.03608	0.03205	0.04799	0.04968	0.05674	0.04819	0.04294

[a] In this table the notation xE+01 = $x \times 10^1$ and xE−01 = $x \times 10^{-1}$ and so on.

Table II. Adsorption Equilibrium Data for Ethylene-Ethane-MSC • 5A

	amount adsorbed, mmol/g of adsorbent		
press., kPa	ethylene	ethane	vap phase comp
	Temperature = 283.15 K		
0.660	0.050	0.648	0.1308
0.659	0.118	0.569	0.2531
0.657	0.171	0.490	0.3723
0.649	0.217	0.410	0.4858
0.639	0.273	0.341	0.5886
0.648	0.338	0.273	0.6849
0.684	0.366	0.198	0.7786
0.651	0.442	0.136	0.8633
0.633	0.495	0.062	0.9410
2.686	0.086	1.048	0.1103
2.738	0.180	0.956	0.2289
2.689	0.282	0.856	0.3401
2.825	0.459	0.636	0.5541
2.692	0.640	0.388	0.7559
2.604	0.982	0.133	0.9326
3.958	0.095	1.245	0.1044
4.006	0.208	1.110	0.2234
3.968	0.323	1.007	0.3330
3.973	0.409	0.871	0.4411
3.936	0.536	0.751	0.5440
4.034	0.658	0.613	0.6490
3.940	0.791	0.476	0.7450
3.928	0.929	0.331	0.8406
4.016	1.032	0.157	0.9275
6.650	0.157	1.435	0.1041
6.703	0.231	1.275	0.2167
6.591	0.364	1.179	0.3235
7.064	0.612	0.886	0.5328
6.573	0.868	0.559	0.7376
6.735	1.293	0.190	0.9249
13.523	0.136	1.701	0.1006
13.467	0.273	1.521	0.2094
13.487	0.424	1.410	0.3137
13.801	0.752	1.100	0.5208
13.379	1.045	0.706	0.7255
13.559	1.565	0.237	0.9198
20.04	0.216	1.883	0.0968
20.06	0.320	1.773	0.2070
19.98	0.463	1.525	0.3110
20.16	0.594	1.349	0.4127
20.13	0.815	1.172	0.5131
19.97	0.984	0.963	0.6190
20.24	1.152	0.795	0.7174
18.89	1.417	0.540	0.8180
19.81	1.660	0.255	0.9144
	Temperature = 293.15 K		
0.640	0.040	0.483	0.1065
0.674	0.087	0.427	0.2389
0.667	0.125	0.369	0.3616
0.665	0.161	0.319	0.4719
0.681	0.197	0.266	0.5818
0.663	0.246	0.214	0.6687
0.669	0.287	0.162	0.7669
0.685	0.332	0.110	0.8554
0.665	0.360	0.054	0.9316
2.002	0.063	0.833	0.1007
2.020	0.134	0.716	0.2270
2.029	0.208	0.645	0.3416
1.936	0.265	0.552	0.4484
1.980	0.349	0.484	0.5537
1.996	0.417	0.390	0.6507
1.988	0.496	0.298	0.7502
1.980	0.558	0.196	0.8406
1.956	0.644	0.099	0.9231
5.315	0.084	1.170	0.0953
5.359	0.192	1.051	0.2151
5.317	0.292	0.950	0.3266
5.399	0.381	0.831	0.4283
5.395	0.504	0.722	0.5236
5.282	0.599	0.592	0.6316
5.231	0.733	0.460	0.7327
5.378	0.850	0.317	0.8289
5.346	0.979	0.159	0.9164
10.650	0.095	1.458	0.0888
10.720	0.230	1.322	0.2096
10.730	0.360	1.190	0.3168
10.640	0.466	1.040	0.4176
10.583	0.609	0.893	0.5212
10.443	0.746	0.759	0.6207
10.928	0.918	0.583	0.7207
10.640	1.072	0.400	0.8199
10.640	1.231	0.200	0.9122
	Temperature = 313.15 K		
0.637	0.026	0.265	0.1308
0.667	0.048	0.250	0.2280
0.679	0.073	0.216	0.3362
0.667	0.092	0.186	0.4488
0.655	0.115	0.155	0.5551
0.696	0.133	0.124	0.6535
0.712	0.162	0.098	0.7471
0.657	0.179	0.063	0.8345
0.663	0.201	0.032	0.9242
3.302	0.059	0.643	0.1217
3.328	0.110	0.603	0.2144
3.329	0.173	0.554	0.3237
3.348	0.226	0.481	0.4284
3.317	0.284	0.406	0.5335
3.341	0.346	0.334	0.6328
3.326	0.413	0.266	0.7313
3.334	0.474	0.177	0.8221
3.345	0.550	0.091	0.9159
9.203	0.091	1.024	0.1172
9.334	0.175	0.966	0.2067
9.527	0.264	0.886	0.3146
9.200	0.345	0.753	0.4165
9.200	0.453	0.653	0.5207
9.235	0.535	0.534	0.6206
9.167	0.641	0.430	0.7198
9.263	0.764	0.294	0.8140
9.572	0.888	0.147	0.9105
22.560	0.166	1.427	0.1145
22.903	0.229	1.321	0.2026
22.575	0.351	1.215	0.3084
22.827	0.483	1.058	0.4088
22.694	0.615	0.897	0.5199
22.920	0.751	0.747	0.6117
22.606	0.913	0.605	0.7110
22.855	1.091	0.407	0.8072
22.654	1.277	0.188	0.9064

was insignificant. The experimental procedure was the same as the one previously reported (*2*), but the experimental time was much shortened by the pump. The total amounts of adsorption were obtained by measurement with the spring balance and by the volumetric method; the adsorption by the latter method was always a little larger because it included the adsorption on the surface of the apparatus and on the vacuum grease. Because the true total amount of adsorption by the carbon molecular sieve was the value obtained by the spring balance and because the amount of each component adsorbed can be obtained by the volumetric method, the difference in the total adsorption between the two methods should be distributed into adsorptions of components 1 and 2. The total difference of adsorption, Δa^t, is the sum of the difference for components of 1 and 2 (eq 1). The ratio of Δa_1 to Δa_2 is proportional to

$$\Delta a^t = \Delta a_1 + \Delta a_2 \tag{1}$$

the ratio of the vapor-phase compositions and to the ratio of the amount adsorbed of component 1 at pure state, a_1^0, to that of component 2, a_2^0, at the same temperature and pressure at which the equilibrium data for the adsorption of the mixture was obtained (eq 2). The ratio a_1^0/a_2^0 had a value of 1.1 and

$$\frac{\Delta a_1}{\Delta a_2} = \frac{a_1^0}{a_2^0}\frac{Y_1}{Y_2} \qquad (2)$$

was rather insensitive to the temperature and pressure. When eq 1 and 2 are combined, Δa_1 can be expressed by eq 3.

$$\Delta a_1 = \frac{\Delta a^t}{1 + \dfrac{a_2^0}{a_1^0}\dfrac{Y_2}{Y_1}} \qquad (3)$$

The true amount of each component adsorbed is the observed value subtracted by Δa_i.

Results

The isothermal data of adsorption for pure components which have been measured in the desorption process are well correlated in log–log form by the polynomial equation of 7th power

$$\log a = \sum_{i=0}^{7} C_i (\log P)^i \qquad (4)$$

where a is the amount adsorbed expressed in mmol/g of adsorbent and P is the pressure in Pa. The coefficients of the equations and the standard deviation expressed in mg/g of adsorbent are listed in Table I. The calculated adsorption isotherms essentially include the unremovable adsorptions whose values averaged over two or three runs are also listed in Table I. The equilibrium data for the binary mixtures are shown in Table II. The composition of ethylene in the adsorbed phase increases with pressure at constant vapor-phase composition. The same effect, but to a lesser degree, is shown with increasing temperature.

Registry No. Carbon, 7440-44-0; ethane, 74-84-0; ethylene, 74-85-1.

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Studies of Proton-Transfer Equilibria of Different Charge Type Acids in the Glycerol–Water Solvent System at 25 °C

Amrita Lal De* and Arup Kumar Atta

Department of Chemistry, Presidency College, Calcutta 700 073, India

First dissociation constants of thymolsulfonephthalein (H_2A), a neutral acid, second dissociation constants of thymolsulfonephthalein (HA^-), a negatively charged acid, and dissociation constants of *m*-nitroanilinium ion (BH^+), a positively charged acid have been determined spectrophotometrically at 25 °C in glycerol–water mixtures containing 10, 30, 50, and 70 wt % glycerol. Standard Gibbs energies of transfer, $\Delta G°_t(B)$, of *m*-nitroaniline (B) from water to mixed solvents have been evaluated from measurement of solubilities at 25 °C. $p({}_sK)_{H_2A}$ increases gradually, but $p({}_sK)_{HA^-}$ increased rapidly with increase in proportion of glycerol in the solvent. In contrast, the corresponding value of BH^+ decreases, passes through a minimum, and then rises very slowly as mole percent of glycerol increases in the solvent. The widely different nature of solvent effect $\delta(\Delta G°) = 2.303RT[p({}_sK)^N - p({}_wK)^N]$ for different charge type acids in this solvent system has been interpreted in terms of various types of interaction of all the species involved in the ionization equilibria with the solvent molecules.

Introduction

It is now a well-recognized fact that dissociation of acids in mixed solvent media is not only a function of the electrostatic effect but is also influenced profoundly by specific solvation of the species involved in the ionization equilibria. In order to understand solvent effect on the dissociation of acid in glycerol (GL)–water solvent system, dissociation constants of three different charge type acids have been measured at 25 °C. First dissociation constants of thymolsulfonephthalein (H_2A), a neutral acid, second dissociation constant of thymolsulfonephthalein (HA^-), a negatively charged acid, and dissociation constants of *m*-nitroanilinium ion (BH^+), a positively charged acid, have been measured in a series of aqueous mixtures of glycerol. The contribution (*1*) of the base, *m*-nitroaniline (B), to the dissociation of the BH^+ acid was determined from the measurement of solubilities in water as well as in various solvent mixtures.

The neutral thymolsulfonephthalein molecule can be written as H_2A since it has two ionizable hydrogen atoms, one of which undergoes ionization in the acid range (step i) and the other in the alkaline (step ii). The two steps may be represented as shown in eq 1.

$$\underset{\text{(red)}}{H_2A} \underset{\text{(step i)}}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{(yellow)}}{HA^-} \underset{\text{(step ii)}}{\overset{-H^+}{\rightleftharpoons}} \underset{\text{(blue)}}{A^{2-}} \qquad (1)$$

Experimental Section

The purification of the solvents glycerol (GL) and water have been described (*2*). Thymolsulfonephthalein (proanalysi, E. Merck) was used without any further purification. *m*-Nitroaniline (A.R.) was purified by two crystallizations from aqueous ethanol (95% v/v) and then dried in vacuo. Tris(hydroxymethyl)methylamine (Tris) (Sigma, reagent grade) was used after recrystallization from 75% methanol. HCl solution was prepared and titrated in the manner already described (*3*).

Since H_2A and BH^+ are relatively strong acids, a considerable variation in the degree of dissociation was achieved by varying the concentration of the added strong acid, HCl, and thermodynamic dissociation constants could be determined without recourse to buffer solutions. In both the cases, a series of solutions were prepared (total volume 10 cm^3) by adding weighed amounts of HCl solutions and the solvents to weighed

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