Adsorption Equilibria of Binary Mixtures of Benzene and Acetone Vapors on Graphitized Carbon Black

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Adsorption isotherms of binary mixtures of acetone and benzene vapors on a graphitized carbon black (GCB) adsorbent were determined at 20 °C. Mass-spectrometric tracer pulse chromatography was used to measure the adsorption of each component at 70 different pressures of acetone and benzene to produce a full three-dimensional isotherm over the range up to, and slightly beyond, monolayer coverage. Each experiment was carried out at a fixed pressure of acetone and different pressures of benzene. The isotherms of benzene, at fixed acetone pressure, were fitted to the BET isotherm equation. Coadsorbed acetone had little or no effect on the benzene isotherms or the BET parameters; however, the isotherms of acetone were significantly influenced by coadsorption of benzene. Even the smallest amount of adsorbed benzene disproportionately diminished the extent of acetone adsorption. The retention volumes of small samples of two additional solutes, *n*-pentane and 1-propanol, were also determined at each isotherm point to determine the effect of the amount and composition of the binary condensed phase on the adsorption and retention of a third adsorbate at infinite dilution.

Introduction

There are innumerable practical applications of gas-solid adsorption equilibria, including environmental sampling, catalytic processes, and the separation and purification of gases. A disparity exists, however, between the practical and theoretical aspects of gas-solid adsorption. Most of the current adsorption models were developed for single-component systems. Unfortunately, most practical applications of adsorbents involve complex mixtures of gases or vapors, and the single-component models are usually inadequate. This is especially the case for strongly interacting adsorbates, such as organic vapors. The lack of good models for complex systems is due in part to the lack of appropriate experimental data for such systems.

The majority of binary systems that have been studied (*1*-*4*) have involved permanent gases, and the experiments have been restricted to fixed total pressure or fixed gas-phase composition. Some investigations have, however, been carried out with organic vapors. For example, Karpinski and Kowalcyzk (*5*, *6*) used a volumetric technique to study the adsorption of mixtures of acetonitrile and several alcohols and amines on graphitized carbon black. The experiments were carried out at fixed vapor-phase composition, and the results showed that adsorption of a binary vapor was almost always less than the adsorption of either pure component at the same relative pressure. Such results are intriguing, but isolated. The limiting factor in the study of such systems is the magnitude of effort required with the common gravimetric and volumetric experimental methods for the study of multicomponent systems. This situation has led to the recent renewal of interest in the use of chromatographic methods for the study of these complex systems.

Kobayashi et al. (*7*) carried out the earliest chromatographic adsorption studies of binary systems using tracer pulse chromatography with radioactive tracers. More recently, Danner et al. (*8*) used the same procedure to study binary mixtures of several permanent gases on zeolites. This work also led to one of the few theories for multicomponent gas-solid adsorption. This "vacancy" theory (*9*, *10*) was adequate to describe the systems studied, although it has been shown to be unsatisfactory for other systems (*11*).

Tracer pulse chromatography with stable isotopes and a mass-specific detection system has recently been used to study binary systems with one component at infinite dilution. This method has been shown to be accurate (*12*). It is very simple both mathematically and experimentally, and it does not require the use of radioactive isotopes. These studies involved both permanent gases (*13*, *14*) and organic vapors (*15*-*17*). The results showed that the effect of one adsorbed component on the adsorption or retention of a second component is usually complex and coadsorption may result in enhanced overall adsorption (cooperativity) or diminished adsorption depending upon the properties of the adsorbent and the adsorbates.

In the present work this tracer pulse method has been used to investigate binary systems with both components at finite concentration. This experimental protocol allows for the development of a full grid of isotherm points for both adsorbates.

Experimental Section

The experimental procedure used in this investigation was the same as that described previously (*12*, *14*) with only minor variations. Small (10 L) individual tanks were prepared of mixtures of helium with acetone or benzene. Helium acted only as a gas-phase diluent, and previous studies (*14*, *17*) have shown that helium has no effect upon the adsorption isotherms of either adsorbate. The composition of each carrier gas mixture was determined by comparison with a standard gas mixture using a Hewlett-Packard (Palo Alto, CA) 5840 gas chromatograph. A Hewlett-Packard 5985 GC/MS system was used for the determination of the adsorption and retention data. Carrier gases containing both acetone and benzene were obtained by mixing the flow from two separate tanks in the injection port of the GC/MS system.

Isotherms were measured at fixed pressures of acetone and differing pressures of benzene. That is, the isotherms of both adsorbates were determined at fixed acetone pressure. This was accomplished by maintaining constant inlet and outlet pressures and constant total flow rate. The pressures of adsorbate were varied by changing carrier gas tanks.

Adsorption data for both adsorbates were determined from the retention volumes of their deuterated analogues. The isotopes used were acetone-d_6 and benzene-d_6 (Commissariat pour l'Energie Atomique, France, 99.8%). The isotopic solutes and the elution solutes, 1-propanol and n-pentane, were injected as vapors at a sample size of less than 1 μmol of each component. Neon was injected with the solutes to determine the dead time and void volume of the system. The specific retention volumes of the elution solutes were corrected to 0 °C and unit surface area of the adsorbent.

The chromatographic columns were constructed of $^1/_8$ in. o.d. stainless steel packed with 60/80 Carbopack C (Supelco, Bellefonte, PA). The surface area, 8.9 m^2/g, was calculated

0021-9568/84/1729-0420$01.50/0

Table I. Isotherm Data for Benzene and Acetone and Retention Volume Data for Infinitely Dilute Solutes on Carbopack C at 20 °C

Pressure of Benzene (torr)	Amount Absorbed (μmol/m^2)		Retention Volume of Solutes (mL/m^2)	
	Benzene	Acetone	Pentane	Propanol
	Acetone Pressure = 4.0 torr			
0.0	0.00	0.73	18.7	15.1
0.1	0.12	0.65	14.5	6.98
0.2	0.27	0.61	5.47	9.66
0.9	0.90	0.47	8.70	5.30
3.6	1.70	0.26	2.80	2.64
6.6	2.85	0.24	2.93	2.64
17.	4.41	0.20	2.78	3.30
24.	4.84	0.15	0.82	2.07
	Acetone Pressure = 5.3 torr			
0.0	0.00	1.19	23.3	13.2
0.1	0.11	0.93	18.4	8.09
0.2	0.26	0.82	15.3	6.94
0.7	0.89	0.74	12.9	5.71
1.3	1.09	0.59	7.10	5.69
2.6	1.77	0.50	6.38	4.71
4.7	2.22	0.36	3.82	2.80
9.4	3.21	0.32	2.39	2.19
12.	3.57	0.31	2.63	2.45
17.	4.16	0.23	1.58	1.80
	Acetone Pressure = 8.8 torr			
0.0	0.00	1.81	20.5	16.0
0.2	0.32	1.35	8.61	12.3
0.4	0.28	0.79	4.65	5.64
0.9	0.80	0.86	5.99	7.03
1.9	1.12	0.74	4.38	4.85
3.7	2.14	0.74	4.36	4.93
6.8	3.09	0.58	3.26	3.83
13.	4.33	0.47	2.05	2.47
24.	5.74	0.39	1.12	2.11
	Acetone Pressure = 9.3 torr			
0.0	0.00	1.67	14.0	19.0
0.1	0.16	1.56	12.4	10.5
0.2	0.29	1.13	7.78	7.22
1.0	0.74	0.80	5.08	4.63
4.0	1.82	0.63	2.83	3.44
7.3	2.58	0.51	1.99	2.57
18.	5.10	0.48	1.97	2.25
26.	5.51	0.37	0.78	2.10
	Acetone Pressure = 14 torr			
0.0	0.00	3.57	12.9	23.4
0.1	0.09	2.51	9.72	11.6
0.2	0.19	1.85	6.64	9.96
0.7	0.56	1.49	4.78	7.07
2.5	1.63	1.26	3.99	6.01
4.7	2.43	1.10	3.52	4.64
9.3	3.09	0.81	2.11	2.83
12.	3.78	0.84	2.40	3.43
17.	3.99	0.61	1.17	2.22
	Acetone Pressure = 27 torr			
0.0	0.00	5.46	6.64	18.3
0.1	0.09	4.11	4.93	13.6
0.3	0.24	3.54	4.77	10.7
1.0	0.87	3.34	4.25	8.58
4.0	2.53	2.70	3.21	6.34
7.4	3.34	1.94	2.37	5.03
15.	4.17	1.30	1.36	2.81
19.	4.67	1.40	1.64	3.75
27.	5.01	1.13	0.86	2.31
	Acetone Pressure = 35 torr			
0.0	0.00	6.84	5.68	18.6
0.1	0.06	3.98	3.49	9.54
0.2	0.14	3.16	2.97	8.59
0.9	0.45	2.62	2.65	6.38
3.5	1.22	2.44	2.08	5.33
6.4	2.32	1.94	1.83	4.38
13.	3.05	1.76	1.05	3.49
16.	4.44	2.17	1.60	4.13
23.	4.52	1.49	0.88	2.49
	Acetone Pressure = 57 torr			
0.0	0.00	7.44	2.25	12.5
0.1	0.02	4.57	1.37	5.80
0.2	0.05	4.18	1.28	5.86
0.7	0.21	3.72	1.21	5.77
2.6	0.78	3.72	1.15	5.53
4.3	1.37	3.56	1.21	4.63
12.	3.08	3.49	1.38	4.28
17.	3.84	3.02	0.66	3.81

from the monolayer capacity determined from the BET (*18*) equation and a specific area for benzene on GCB of 43.2 Å^2 (*19*). These values are in excellent agreement with the literature values 9 (*20*) and 9.1 (*21*) m^2/g measured with a specific area of 47.2 Å^2 for benzene (*21*). All of the experiments were carried out at 20 °C.

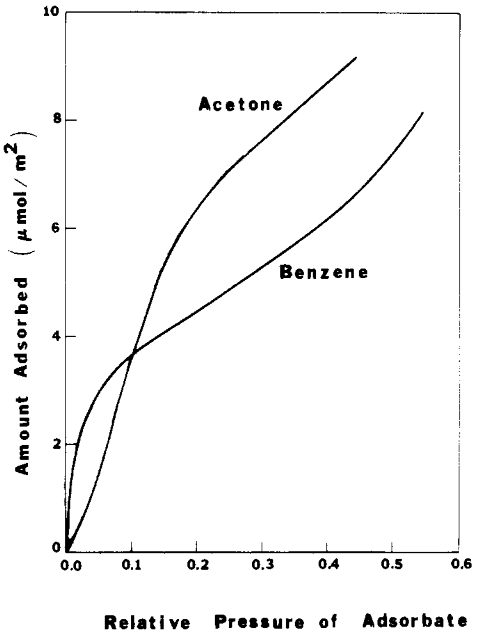

Figure 1. Generalized isotherms from the literature (*15*, *17*, *22*) for pure benzene and acetone on Carbopack C.

Table II. BET Parameters for the Isotherms of Benzene on Carbopack C at 20 °C and Various Partial Pressures of Acetone

acetone press., torr	BET parameters for benzene: v_m, μmol/m^2	BET parameters for benzene: C
0.0	3.8	83
4.0	3.7	25
5.3	3.6	25
8.8	4.5	15
9.3	4.1	16
14.	3.7	23
27.	3.6	29
35.	4.0	11
57.	4.9	5.4

Results and Discussion

Several investigators (*15*, *17*, *22*) have measured the adsorption isotherms of the pure components (acetone or benzene) on GCB at 20 °C. The literature data for each system are in excellent agreement. Representative plots of the best line fits for the adsorption of each component as a function of relative pressure ($P/P°$) are given for these data in Figure 1. The data points have been omitted for clarity; however, the curves show that benzene is more strongly adsorbed at low pressures while the converse is true at higher pressures. The experimental data for the adsorption of pure benzene on GCB (*17*, *22*) fit the BET equation with a calculated monolayer capacity of 3.8 μmol/m^2. However, the acetone data (*15*) did not fit any of the classical equations. The isotherm was essentially linear, but segmented into two distinct portions with the break point corresponding to the point of formation of a monolayer, assuming a specific surface area of 25 Å^2 for acetone on GCB.

The measured adsorption and retention data for the binary systems at 20 °C are given in Table I. As previously pointed out, the experiments were carried out at fixed acetone pressures. This was the most convenient method because the benzene isotherms followed a well-established isotherm equation whereas the acetone isotherms could not be fitted to a model with meaningful parameters. The effects of adsorbed acetone on the BET C and v_m parameters for benzene are given in Table II. The v_m parameters are relatively constant; however, there is some systematic variation. There are local maxima at intermediate acetone pressures (8.8 and 9.3 torr) and at the highest pressures (35 and 57 torr). The latter two pressures represent relative pressures lying beyond the crossover point in Figure 1, i.e., pressures that would be sufficient for the formation of a monolayer of acetone *in the absence of coadsorbed benzene*. The slightly enhanced adsorption or cooperativity at pressures close to 9 torr was verified by repeated measurements at 8.8 and 9.3 torr. Similar cooperativity has been observed in other systems with one component at inifinite dilution (*15*–*17*), and the usual explanation is that lateral interactions between adsorbates at less than monolayer coverage can result in enhanced adsorption in this region.

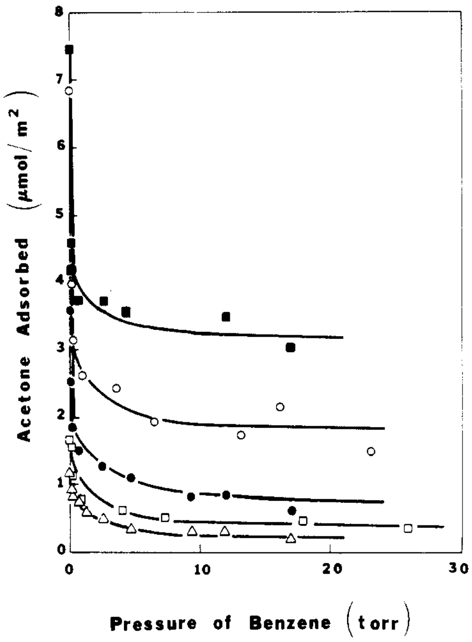

Figure 2. Adsorption of acetone on GCB at 20 °C as a function of benzene pressure at several acetone pressures: (△) 5.3, (□) 9.3, (●) 14, (○) 35, and (■) 57 torr.

At the highest acetone pressures ($P > 30$ torr) the v_m values appear to be unrealistically high. This is due to interference between the adsorbates which influenced the shape of the benzene isotherms. The benzene isotherms were almost linear at these pressures and the BET parameters were less reliable. However, even at the highest acetone pressures the effect of acetone on the adsorption of benzene was surprisingly small.

On the other hand, the effect of coadsorbed benzene on the acetone isotherms is unusually significant. This interference effect is shown in Figure 2, which is a plot of the amount of acetone adsorbed (at fixed acetone pressure) as a function of the pressure of benzene. Large amounts of acetone are displaced from the adsorbent surface at very low pressures of benzene. A single benzene molecule can displace up to 50–100 molecules of acetone from the surface at the lowest benzene pressures. Such magnification effects have not been previously observed for physical adsorption on GCBs; however, similar effects have been observed for chemisorption on metal catalysts. For example, Chen and White (*23*) recently reported a ratio of 250:1 for the inhibition of hydrogen adsorption on Pt by the presence of adsorbed K. The exact mechanism that leads to such magnification effects is not clear (*23*, *24*); however, studies of physical adsorption may serve as a model for adsorption on catalytic systems which are far more complex.

Registry No. Acetone, 67-64-1; benzene, 71-43-2; *n*-pentane, 109-66-0; 1-propanol, 71-23-8.

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Received for review October 17, 1983. Accepted May 11, 1984. Acknowledgment is made to the National Science Foundation and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Osmotic Coefficients of Trialkyl Phosphates in Water†

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Osmotic and activity coefficients are reported at several temperatures for triethyl phosphate (TEP) and tripropyl phosphate (TPP) at low concentrations in water. TEP forms solutions that do not depart from ideality as much as do those formed from TPP. At 15 °C the total excess Gibbs energies were −11 and −32 J·kg^{-1} at 0.05 mol·kg^{-1} for TEP and TPP, respectively. For TEP, the nonidealities resulted from a balance between entropic and enthalpic effects.

Introduction

Neutral organic phosphates are frequently used as extractants in the reprocessing of irradiated nuclear fuel (*1*). We are presently engaged in a program to study the adsorption of such extractants at oil/water interfaces (*2*, *3*) and, to interpret our adsorption results, activity coefficients of the solutes in both the oil and the water are required. This work reports osmotic and activity coefficients of two of the lower trialkyl phosphates, triethyl phosphate (TEP) and tripropyl phosphate (TPP), in water.

Experimental Section

Osmotic coefficients were measured at various temperatures by using a Corona/Wescan Model 232 A vapor pressure osmometer. The general principles and operation of this instrument have been described fully by Burge (*4*) and our procedures have been described previously (*5*).

At each measurement temperature the osmometer was calibrated against standard solutions of mannitol in water. The voltage difference between the two thermistors, ΔV, was divided by the mannitol molality, m, and $\Delta V/m$ was plotted against m. Since these solutions are close to ideal, straight lines were obtained with small slopes. The value of $\Delta V/m$, extrapolated to zero molality, was taken as the reference value, $(\Delta V/m)_r$.

Table I. Constants of Eq 2 for Osmotic Coefficients of TEP and TPP in Water

T, °C	no. of points	A_1, kg·mol^{-1}	A_2, kg·mol^{-1}	10^3(rsds)[a]
		TEP		
15	19	16.7 ± 5.2	19.1 ± 5.7	3.06
20	36	55.5 ± 13.9	62.4 ± 15.2	7.91
25	23	37.4 ± 7.5	43.8 ± 8.4	4.02
30	18	134.0 ● 39.4	154.1 ± 44.5	3.68
		TPP		
7.5	18	24.5 ± 8.6	30.9 ± 9.6	2.36
15	21	104.6 ± 29.9	124.8 ± 33.9	5.28

[a] Residual sum of deviations squared.

The sources and purification of TEP, TPP, and water have been described (*3*). The mannitol was ACS reagent grade, and it was dried at 110 °C and stored in a desiccator.

Results and Discussion

Osmotic coefficients (ϕ) were calculated by using the equation

$$\phi = (\Delta V/m)/(\Delta V/m)_r \qquad (1)$$

where ΔV is the voltage difference required to maintain a steady bridge current across the thermistors (*4*, *5*) and m is the solute molality. The reference values, $(\Delta V/m)_r$, were those obtained from the mannitol reference solutions extrapolated to infinite dilution, as noted above. This equation assumes that the practical osmotic coefficient, ϕ, for the reference solution at infinite dilution is 1.000.

The original osmotic coefficients are provided as supplementary material. (See paragraph at the end of text regarding supplementary material.) Osmotic coefficients for TEP were measured at 15, 20, 25, and 30 °C. However, for TPP they could only be measured at 7.5 and 15 °C. At higher temperatures, stable readings could not be obtained, probably because of the high volatility of the TPP. Since TPP is only sparingly soluble in water, even low concentrations give a high percentage of the equilibrium vapor pressure of the pure liquid over

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† Issued as AECL-8097.

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