tained by drawing a straight line from the origin to the point determined by measurement of the total quantity of electricity, represents the number of moles of hydrogen which would be expected for cathodic evolution. This straight line, incidentally, coincides satisfactorily with one calculated from the measured current intensity, which was held at a constant value throughout the run.
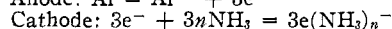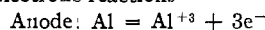
These data on gas evolution may be interpreted in the following manner. Although the final result of the reduction reaction at the cathode is the liberation of the theoretical amount of hydrogen, the time lag in the evolution indicates that this is not the primary electrode process. Apparently the primary cathode reaction is the formation of a reducing agent which is capable of existing in solution for some time before it eventually reacts with the solvent. Since this time lag is observed only when the colored substance formed at the cathode is persistent, the reducing power of the solution evidently should be attributed to the same component which is responsible for the color.

The distinguishing characteristics of the cathode phenomenon may be summarized: (1) A blue color is formed at the cathode surface, and intensely colored blue solutions are obtained. (2) The rate of disappearance of color increases in the presence of iron or iron oxide. (3) The formation of colored solutions is accompanied by an increase in electrical conductivity. (4) The number of moles of hydrogen evolved from the beginning of electrolysis to complete disappearance of color from the solution is equal to the number of moles calculated on the assumption of cathodic evolution of hydrogen, but the time lag in this process indicates that such evolution is not the primary electrode reaction.
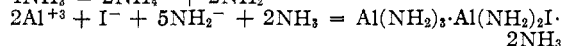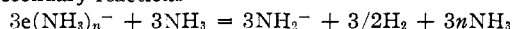
These characteristics may all readily be explained in terms of the theory that the primary cathode process is the dissolution of electrons into the solution. In accordance with this theory, the electrode reactions and subsequent reactions in the solution may be formulated as

Electrode reactions

Anode: $Al = Al^{+3} + 3e^-$
Cathode: $3e^- + 3nNH_3 = 3e(NH_3)_n^-$

Secondary reactions

$3e(NH_3)_n^- + 3NH_3 = 3NH_2^- + 3/2H_2 + 3nNH_3$
$4NH_3 = 2NH_4^+ + 2NH_2^-$
$2Al^{+3} + I^- + 5NH_2^- + 2NH_3 = Al(NH_2)_3 \cdot Al(NH_2)_2I \cdot 2NH_3$

The blue solid which is formed at low temperatures may possibly be a solid ammoniate, similar to the previously described ammoniates of calcium, strontium and barium.[6] However, the conditions under which this blue solid is formed are such that the results of any attempts at analysis would be inconclusive.

Summary

The results of the electrolysis of solutions of aluminum iodide in liquid ammonia may readily be explained on the hypothesis that the blue solutions formed result from a cathode reaction consisting in dissolution of electrons, which are capable of existing in the presence of a considerable concentration of Al^{+3} ion. The blue solute consists, therefore, of ionized metallic aluminum in liquid ammonia. The ammoniated electron reacts with the solvent to form amide ion and liberate hydrogen.

(6) Biltz and Huttig, Z. anorg. Chem., **114**, 241 (1920).

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Adsorption Equilibria of Liquid Mixtures of Benzene and Methanol with Charcoal

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The vapor adsorption study of this system was reported in a previous paper.[3] The present work concerns the liquid adsorption equilibria. The approach used is largely the same as employed in studying the system CCl_4–CH_3OH on charcoal.[4]

Experimental

Materials.—The materials used for all measurements reported here were the same as used for the vapor adsorption study on this system except that the charcoal was powdered and sieved to a size smaller than 30 mesh.

Direct Measurements of Selective Adsorption. The same method used for earlier work[4] without pre-evacuation of charcoal was employed. Concentration change was determined by use of a Pulfrich temperature controlled refractometer.

Data and Discussion

Direct Measurements.—The results of these experiments are plotted in Fig. 1. The agreement of these data with other data reported by Bartell and Sloan[5] for this system (though not

(1) From a dissertation submitted by R. B. Olney to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Master of Science Degree, August, 1942.

(2) American Cyanamid Company, Stamford, Conn.

(3) H. H. Rowley, R. B. Olney and W. B. Innes, J. Phys. & Colloid Chem., in press.

(4) W. B. Innes and H. H. Rowley, J. Phys. Chem., **51**, 1173 (1947).

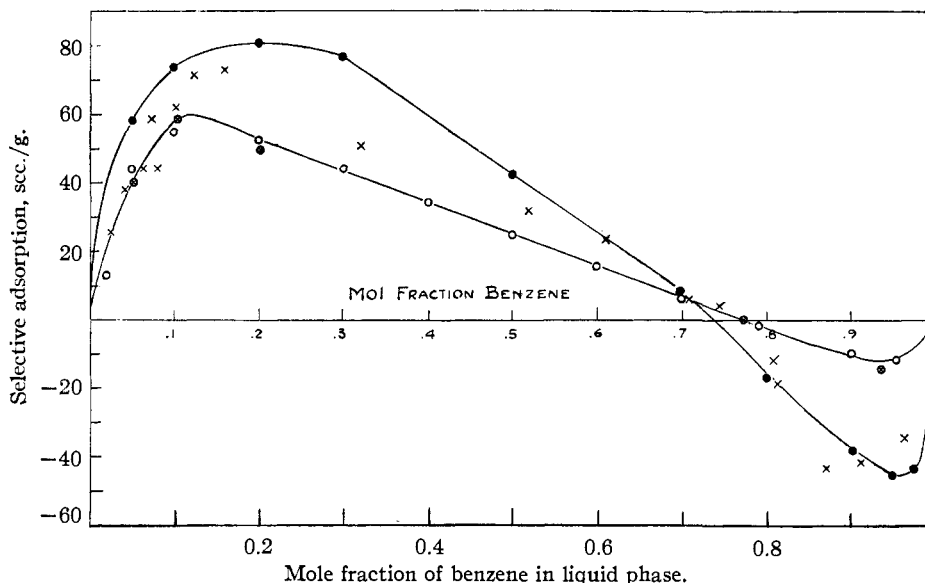(5) F. E. Bartell and C. K. Sloan, THIS JOURNAL, **51**, 1654 (1929).

Fig. 1.—Selective adsorption of C_6H_6, obtained by different methods: $\times$, direct measurements, this work; $\bullet$, direct measurements, Bartell and Sloan, smoothed data; O, $\phi(n_b^s - n_b^L)$; $\otimes$, thermodynamic evaluation.

with the same charcoal) is good. However, the agreement with the selective adsorption determined by the other methods, as described below, differs as to the degree of selective adsorption of methanol at high concentrations of benzene. It is possible that this discrepancy can be attributed to vapor losses,[4] and that the directly measured selective adsorption values are in error in this region.

Evaluation of Selective Adsorption from Mixed Vapor Adsorption Data.—The mixed vapor adsorption data[3] where equilibrium with a liquid phase is being approached make possible the approximate evaluation of n^s, n_a^s and n_a^L and, hence, the selective adsorption, $n\Delta n_a^L$, by means of the equation

$$n \Delta n_a^L = -n^s(n_a^s - n_a^L) \qquad (1)$$

where

Δn_a^L = change in mole fraction of the first component due to adsorption

n^s = total number of moles adsorbed per gram of adsorbent

n_a^s = mole fraction of first component (methanol) in surface phase at equilibrium

n_a^L = mole fraction of first component in liquid phase at equilibrium

n = total moles in both phases per gram of adsorbent

The measurement of the vapor isotherms was carried out in such a manner that n_a^s was known and approximately constant up to at least $n^s = \phi$ which is the amount adsorbed at the point of inflection of the isotherm. Beyond this point, a small amount of capillary condensation or multilayer adsorption is indicated which complicates matters. If, as seems likely, only the monolayer adsorption is selective, the quantity n^s in equation (1) may be identified with the quan-

tity ϕ. The quantity ϕ has previously[3] been determined as a function of n_a^s.

If no capillary condensation or multilayer adsorption occurred, n_a^L could be determined from the saturation pressure point of the isotherm since the saturation pressure is a known function of the liquid composition. Since this is not quite the case, the condensation pressures at the "ϕ point" have been utilized instead to evaluate n_a^L approximately. The selective adsorption values calculated using equation (1) and the forementioned values of ϕ, n_a^s and n_a^L are given in Table I and in the plot of Fig. 1.

TABLE I

CALCULATION OF THE SELECTIVE ADSORPTION OF BENZENE

n^L_b	ϕ scc. (smoothed data)	n_b^s (smoothed data)	$\dfrac{\phi(n_b^s - n_b^L)}{(\text{scc.})}$
0.00	230	0.00	0
.05	145	.35	44
.10	118	.57	55
.20	108	.67	53
.30	106	.72	44
.40	105	.73	35
.50	105	.74	25
.60	105	.75	16
.70	105	.76	6
.80	105	.78	-2
.90	104	.80	-10
.95	103	.83	-12
1.00	95	1.00	0

Values of surface and vapor composition are plotted in Fig. 2.

Thermodynamic Evaluation of Selective Adsorption.—Equilibrium between liquid, vapor
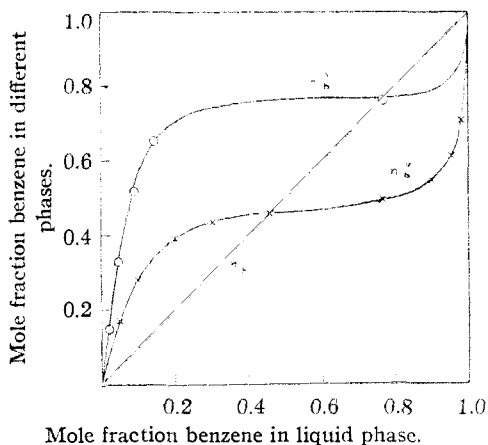
Fig. 2.—Phase composition plots for C_6H_6–CH_3OH at 25°.

The spreading pressures have previously been evaluated for complete isotherms up to saturation pressures.[3] The values at saturation pressures as a function of n_a^L and n_a^s are given in Fig. 3. The partial pressures at saturation are also known and probably closely approximate fugacities and, hence, chemical potentials may be approximately evaluated. Therefore, it is possible to calculate the selective adsorption, $-n^s(n_a^s - n_a^L) = n\Delta n_a^L$, by use of equation (2) and its complement.[4] This has been done and the results obtained are plotted in Fig. 1 where they are compared with those obtained by the other methods. It may be noted that the maximum in the spreading pressure plot, Fig. 3, corresponds with the zero selective absorption, Fig. 1, as expected.
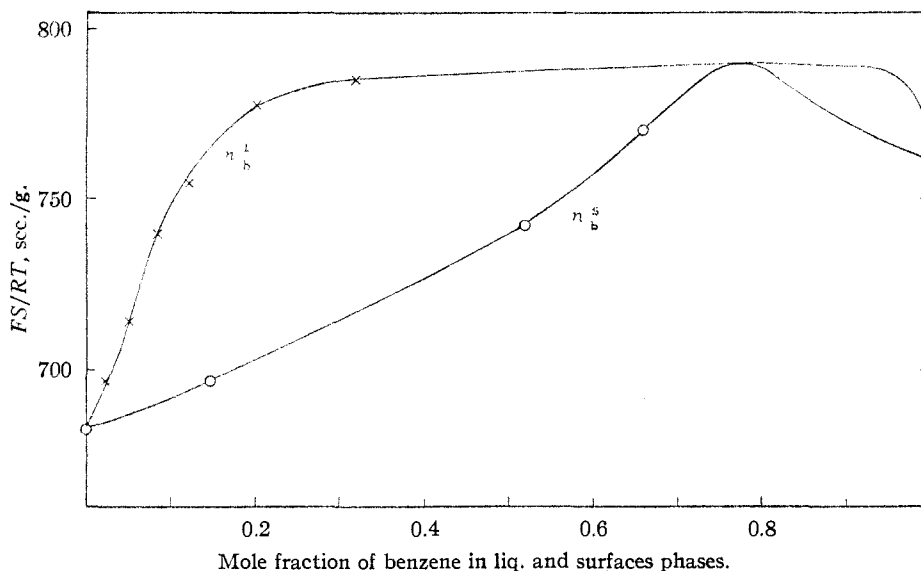

Fig. 3.—Variation of total spreading pressure coefficient with liquid and surface composition.

and surface phases have previously been considered,[6] and the following relation involving $n^s(n_a^s - n_a^L)$ was derived

$$S\left(\frac{\partial F}{\partial \mu_1}\right)_T = \frac{n^s(n_a^s - n_a^L)}{n_b^L} \qquad (2)$$

where F = spreading pressure
  μ_1 = chemical potential of the first component
  S = area of surface per gram of adsorbent

(6) W. B. Innes and H. H. Rowley, J. Phys. Chem., 49, 411 (1945).

Summary

The selective adsorption evaluated by two independent methods as a function of liquid composition is compared with directly measured values. Reasonable agreement is obtained. Surface composition and spreading pressure data are given.