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## ADSORPTION FROM *n*-HEXANE-BENZENE MIXTURES

R. L. MADAN\*, N. K. SANDLE AND J. S. TYAGI\*\*

*Chemistry Department, Indian Institute of Technology, Delhi (India)*

### ABSTRACT

Two samples of tin oxide, in the form of gel and precipitate have been prepared. Their surface properties like surface area, pore structure and surface acidity have been studied. Adsorption from *n*-hexane-benzene mixtures on these oxides reveals that *n*-hexane is preferentially adsorbed. This is explained in terms of low density of polar sites on the surface responsible for the adsorption of benzene molecule. It is observed that the surface of the tin oxide precipitate is more polar than the gel. In the case of tin oxide gel the porosity is also contributing to the preferential adsorption of *n*-hexane. Isotherms of concentration change are analysed by Schay-Nagy and Everett methods to yield the amounts of individual components in the adsorbed phase.

### INTRODUCTION

ADSORPTION from binary solutions of non-electrolytes has been used to characterise the nature of the surface including polarity, distribution and density of active sites and heterogeneity of the surface<sup>1-5</sup>. *n*-hexane-benzene is an interesting mixture for such investigations in view of the comparable areas but different geometrical disposition of the components. Kiselov and Pavlova<sup>6</sup>, from their adsorption studies on Linde molecular sieve 5A, using this liquid mixture, observed that *n*-hexane was completely taken up by the solid and benzene was excluded. They explained their result by assuming that the openings of the pores in Linde molecular sieve 5A were too small to admit molecules of benzene, but molecules of *n*-hexane were admitted in the vertical position. Zhdanov *et al.*<sup>7</sup> studied the adsorption of *n*-hexane-benzene mixtures on the zeolites and found that the interaction between the  $\pi$  electrons of the benzene ring and the ionic lattice of the zeolite was so strong that *n*-hexane was completely excluded over virtually the whole range of concentration. Exhaustive

investigations on a variety of solids is therefore necessary before we can know the circumstances favouring the adsorption of these components on the surface. The adsorption of *n*-hexane-benzene on tin oxide in the form of gel and precipitate is presented in this paper with a view to studying the influence of the structure of the adsorbent on the nature of adsorption. A study of this oxide system is of particular interest as the oxide is a semi-conductor<sup>8</sup> and an active catalyst for the oxidation of hydrocarbons<sup>9</sup>.

### MATERIALS AND METHODS

*Tin Oxide Gel.*—Equal volumes of 1.2 N ammonium hydroxide and 1.0 N stannic chloride solutions were mixed by vigorous shaking and the gel formed was allowed to settle overnight. The gel was washed several times with distilled water and then dried at 30° C and finally crushed to pass through a 100 mesh sieve.

*Tin Oxide ppt.*—Stannic oxide was prepared by the action of tin on con. nitric acid. The oxide was washed with distilled water to make it free from nitrate ions. It was dried at 120° C.

### Surface Area and Pore Structure

Surface area of the samples was determined by adsorption of nitrogen at -183° C using a volumetric apparatus. Pore structure was determined

\* Present Address: Chemistry Department, Government College, Faridabad (India).

\*\* Present Address: Chemistry Department, Meerut College, Meerut (India).

using a mercury porosimeter. The results are given in Table I.

TABLE I A

Solid	Surface area	Surface acidity m eq/g	Pore vol. cc/g	Porosity cc/100 cc
Tin oxide gel	160 m <sup>2</sup> /g	0.21	0.18	50.5
Tin oxide ppt	100 m <sup>2</sup> /g	0.53	..	..

TABLE I B

*Pore size distribution for the gel*

Pore size (Å) (diameter)	% by volume
4-175	72.1
175-300	0.9
300-400	0.0
400-500	0.3
500-75000	26.7

The tin oxide ppt. is assumed to be non-porous and hence these data are not given.

*Surface Acidity.*—The samples (1 g) of the solid were shaken with 20 ml of *n*-butylamine solution of varying concentrations for 24 hours. After separating the solid, the filtrates were titrated with standard hydrochloric acid using bromocresol indicator. Blank solutions without the sample were also treated similarly. Difference in the titre values gave the surface acidity of the samples. These are given in Table I.

### Adsorption Measurement

1 g of the solid was taken in each of the stoppered bottles along with 10 ml of *n*-hexane-benzene mixture of varying compositions and kept at 35° C for 48 hours, with occasional shaking. Blank solutions, without the solid were also treated similarly. Solutions were analysed refractometrically. Isotherms of concentration change were drawn as described by Kipling<sup>1</sup>.

### RESULTS AND DISCUSSION

Table I gives the surface areas, surface acidity (*n*-butylamine adsorption value) of the two samples and the pore structure of the tin oxide gel. Figure 1 gives the composite isotherms, *i.e.*, plots of  $n_0 \Delta x_1 / m$  and  $x_1$  where  $\Delta x_1$  is the change in the mole fraction of *n*-hexane,  $n_0$  the moles of the benzene-*n*-hexane in contact with *m* g of the solids. It is seen that the isotherms for both the solids are U-shaped, *i.e.*, *n*-hexane is preferentially adsorbed on the oxide gel and the oxide ppt. over the entire concentration range. The solids have a heterogeneous surface with polar sites of the oxide. Because of the interaction of  $\pi$  electrons, the polar sites take up benzene while *n*-hexane is taken up by the non-polar sites. The larger non-polar surface is accommodating *n*-hexane, resulting in its higher adsorption. As the surface of tin oxide ppt. is more polar (Table I), benzene is adsorbed to a greater extent as compared with the oxide gel.

TABLE II

*Adsorption from binary mixtures of n-hexane (1)-Benzene (2) at 35° C*

Adsorbent	$x_1$	$n_0 \Delta x_1 / m$ millimoles/g	$\frac{x_1 x_2}{n_0 \Delta x_1 / m}$	Ka	$n^\sigma$ (Everett) millimoles	$n^\sigma$ (Schay-Nagy) Intercept method millimoles
1	2	3	4	5	6	7
Tin oxide gel	0.1	0.11	0.82			
	0.2	0.18	0.86			
	0.3	0.20	1.05			
	0.4	0.18	1.33	4.75	0.53	0.44
	0.6	0.15	1.60			
	0.8	0.08	2.00			
	0.9	0.04	2.25			
Tin oxide ppt	0.1	0.11	0.8			
	0.2	0.14	1.1			
	0.3	0.15	1.6	6.50	0.36	0.28
	0.4	0.14	1.7			
	0.6	0.11	2.2			
	0.8	0.06	2.7			
	0.9	0.03	3.0			

TABLE III

Everett and Schay-Nagy analyses of adsorption from mixtures of *n*-hexane (1)-benzene (2) at 35° C

Adsorbent	$x_1$	$x_1^\sigma$ (Everett)	No of millimoles in the adsorbed layer (Everett)		No. of millimoles in the adsorbed layer (Schay-Nagy)	
			$n_1^\sigma$	$n_2^\sigma$	$n_1^\sigma$	$n_2^\sigma$
Tin oxide gel	0.1	0.35	0.18	0.35	0.16	0.35
	0.2	0.54	0.28	0.25	0.28	0.20
	0.3	0.66	0.34	0.19	0.34	0.13
	0.4	0.76	0.40	0.13	0.36	0.10
	0.6	0.87	0.46	0.07	0.41	0.04
	0.8	0.95	0.50	0.03	0.43	0.01
	0.9	0.98	0.52	0.01	0.44	0.01
Tin oxide ppt	0.1	0.40	0.22	0.14	0.14	0.18
	0.2	0.60	0.22	0.14	0.20	0.10
	0.3	0.73	0.26	0.10	0.23	0.06
	0.4	0.82	0.30	0.06	0.26	0.03
	0.6	0.90	0.32	0.04	0.28	0.01
	0.8	0.96	0.35	0.01	0.29	0.01
	0.9	0.98	0.35	0.01	0.29	0.001

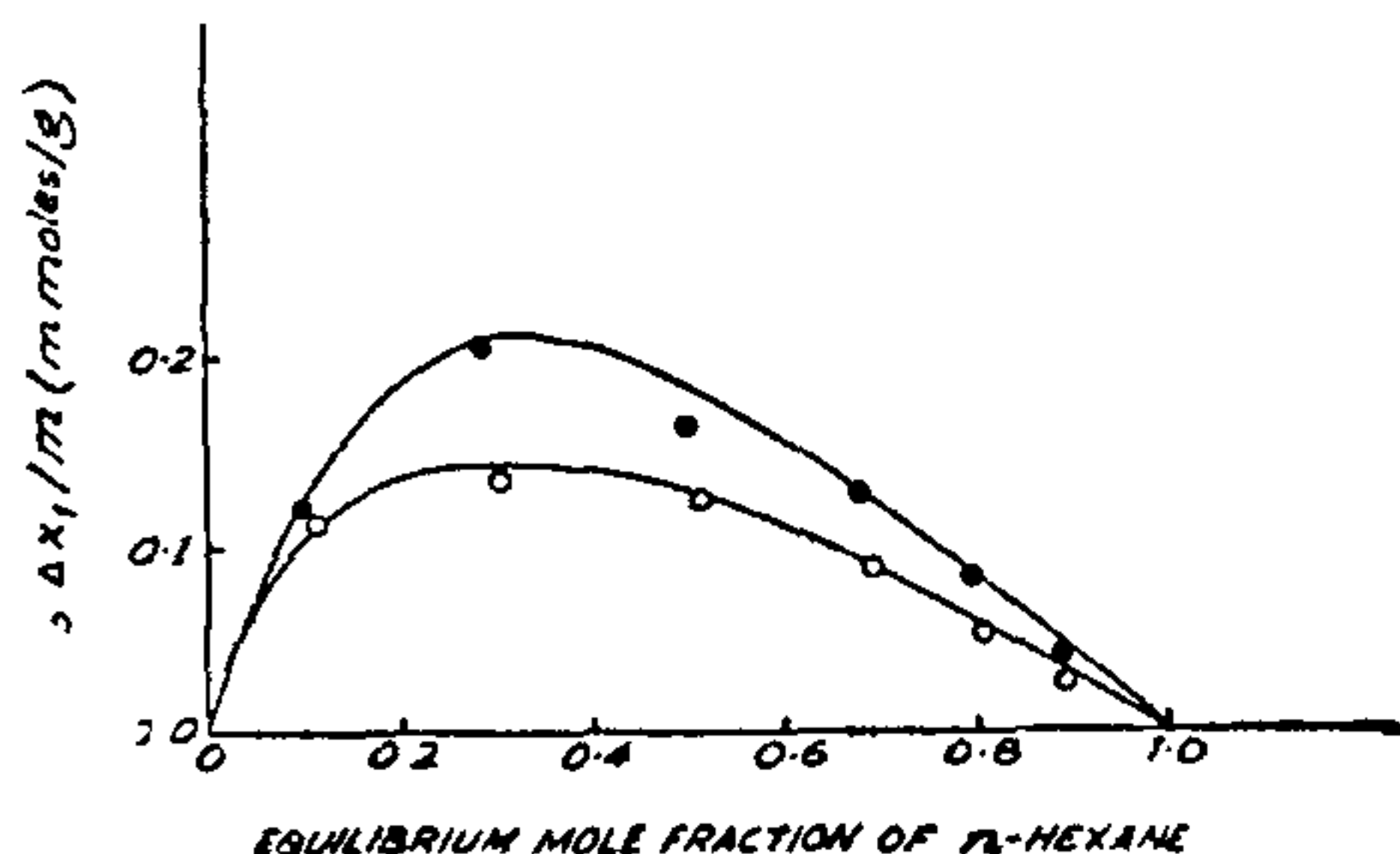


FIG. 1. Composite isotherms for adsorption from *n*-hexane-benzene mixture. ● Tin oxide gel; ○ Tin oxide ppt.

In the case of tin oxide gel, the pore structure also seems to contribute to the preferential adsorption of *n*-hexane. About three-fourths of the pore volume of the gel is in the range 4-175 Å. As the pores having dimensions of nearly 5 Å can take up only *n*-hexane, preferential adsorption of this component is not difficult to explain. The maximum values of  $n_0 \Delta x_1/m$  are 0.2 and 0.14 m moles/g for the gel and the ppt. respectively. The adsorbed layer has been analysed by the models suggested by Schay-Nagy<sup>10-12</sup> and Everett<sup>13-14</sup>. According to Schay-Nagy, the linear portion of the curve when extended to  $x_1 = 0$  and  $x_1 = 1$  axes gives intercepts which correspond to  $n_1^\sigma$  and  $n_2^\sigma$ , i.e., the number of moles of components 1 and 2 in the

adsorbed phase in the concentration range where the isotherm is linear. This can lead us to the total number of moles in the adsorbed phase and then the isotherms can be analysed to give the individual adsorption values of the two components by means of the following equations :

$$n_0 \Delta x_1/m = n_1^\sigma x_2 - n_2^\sigma x_1 \quad (1)$$

$$\frac{n_1^\sigma}{(n_1^\sigma)_m} + \frac{n_2^\sigma}{(n_2^\sigma)_m} = t \quad (2)$$

$x_1$  and  $x_2$  are the mole fractions of *n*-hexane and benzene respectively in the liquid phase.  $n_1^\sigma$  and  $n_2^\sigma$  denote the number of individual components adsorbed  $(n_1^\sigma)_m$  and  $(n_2^\sigma)_m$  are the monolayer values of the solid for the two components. These are obtained by dividing the surface area of the solid by the molecular area of the adsorbate. Molecular areas in our case have been taken from the values reported in the literature<sup>15</sup> and  $t$  is the thickness of the adsorbed layer.

The other way of analysing the adsorbed phase, due to Everett, is given in terms of equations

$$\frac{x_1 x_2}{n_0 \Delta x_1/m} = \frac{m}{n^\sigma} \left( x_1 + \frac{1}{K_a - 1} \right) \quad (3)$$

$$n_0 \Delta x_1/m = n^\sigma (x_1^\sigma - x_1)/m \quad (4)$$

where  $K$  is the distribution constant, other notations have the same meaning as given earlier. The slope and the intercept of the plot of  $x_1 x_2 / (n_0 \Delta x_1/m)$  against  $x_1$  leads to the value of  $n^\sigma$  (the number of moles in the adsorbed layer) and  $K_a$  (the distribution constant).

Everett values of  $n^{\sigma}$  in the present investigation are 0.53 and 0.36 millimole for the gel and the ppt respectively. These values are in the ratio of the surface area of the solids. The monolayer values based on  $50 \text{ \AA}^2$  as the molecular area of  $n$ -hexane are 0.52 and 0.33 millimole. Thus the surface is completely covered during adsorption from this mixture. Possibility of perpendicular orientation of  $n$ -hexane is ruled out because  $50 \text{ \AA}^2$  is the molecular area in parallel orientation. Schay-Nagy values are slightly smaller. Table II gives the distribution constant  $K_a$  for the two solids. Individual adsorption of each component, calculated by the Schay-Nagy and Everett methods over the entire concentration range, is compared in Table III.

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## ON $A^{II}B^{IV}C_2^V$ TYPE MATERIALS

SUBHASH H. RISBUD

*Inorganic Materials Research Division, Lawrence Berkeley Laboratory and Department of Materials Science and Engineering, University of California, Berkeley, California 94720, U.S.A.*

### ABSTRACT

Attention is drawn to current developments in the materials technology of chalcopyrite type  $A^{II}B^{IV}C_2^V$  compounds. The problems associated with synthesis, characterisation, and crystal growth techniques are discussed in relation to the crystal structure. The tendency of selected compounds of this family to form ternary glasses which crystallise at relatively low temperatures is reviewed. Potential applications in the field of non-linear optics, switching devices, and glassy semi conductors are outlined.

### I. INTRODUCTION

THE development of a series of chemical compounds comprising elements of the II-IV-V groups has been at the forefront of technological "action" in the field of Material Science in recent years<sup>1,2</sup>. This interest has been stimulated by the possibility of several applications in areas such as glassy semiconductors<sup>3</sup>, non-linear optics<sup>4,5</sup> and growth of heterojunctions<sup>6</sup>. The successful use of these materials has been hampered, however, because of the lack of readily available high quality single crystals. Single crystals are necessary to perform experiments without the complicating and often uncertain effects of the grain boundaries. With the rapidly emerging potential of these materials, an intensive effort is underway in Materials Research Laboratories around the world to develop techniques of synthesis, characterisation, crystal growth and studies of glass-crystal transformations. It is the intent of this review to outline some of these developments.

### II. SYNTHESIS OF MATERIALS

(a) *Direct Fusion*.—The most commonly used method of synthesis is to seal the required amounts of the elements in evacuated quartz ampoules and heat at a relatively slow rate to one to two hundred degrees above the melting point of the compound; this prevents buildup of any high pressure volatile constituents (especially arsenic and phosphorus). To ensure homogenization of the melts, a vibratory rocking furnace may be used. For arsenides it may be necessary to apply a counter pressure of about 2 atmospheres of argon<sup>7</sup>. Following homogenization for several hours, the ampoule with contents is either cooled by shutting off the furnace or quenched directly in ice water. The synthesised materials are often crushed and remelted a number of times to ensure uniformity.

(b) *Glass Preparation*.—Although glass formation is well known in oxides<sup>8</sup> and chalcogenides<sup>9</sup>, the possibility of the compounds yielding glasses was first explored by Vaipolin *et al.*<sup>10</sup>. These workers