HYDROGEN SOLUBILITY IN ORGANIC SOLVENTS AND ADSORPTION FROM THEM ON CATALYST SURFACE

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The effect of solvent on the adsorption of hydrogen on the surface on platinum catalyst was studied. The adsorption coefficient of hydrogen was found independent of the solvent used. The solubility of hydrogen was determined in 15 solvents.

In most works dealing with the solvent effect on the kinetics of heterogeneous catalytic hydrogenations, the possible effect of solvent on the adsorption coefficient of hydrogen K_H has been ignored. A number of authors have found that in liquid phase catalytic hydrogenations the reaction order with respect to the substrate is zero and that with respect to hydrogen equals unity[1], which is consistent with the rate equation

$$r = kK_H c_{H,bulk} , \tag{1}$$

a simplified form of a more complex Langmuir-type kinetic equation[2]. If allowance is to be made for the effect of solvent, the influencing of all of the three right-side factors of Eq. (*1*) must be taken into account. The aim of most works dealing with this topic has been to establish the effect of solvent on the rate constant k or on the adsorption coefficient K_H, which can only be done if the effect on the bulk concentration is eliminated. The bulk concentrations of hydrogen, given by the Bunsen absorption coefficient values α_S, are lacking for a number of solvents. For this reason, the α_H values were determined in the present work for 15 solvents. In addition, the solvent effect on the adsorption coefficient of hydrogen,

$$K_H = c_{H,surf}/c_{H,bulk} \tag{2}$$

was also studied.

EXPERIMENTAL

Chemicals. All the solvents were freshly distilled with palladium catalyst prior to use to remove the possibly present catalytic poisons. The catalyst of 5% platinum on Supersorbon Degussa HB3 activated carbon (GFR) was prepared by the common procedure[3] from hexachloroplatinic acid; grain size below 0·056 was picked for use.

TABLE I

Measured values of Bunsen absorption coefficient α_S

Solvent	α_S ml/ml
n-Pentane	0·134
n-Hexane	0·120
Tetrahydrofuran	0·083
Ethylbenzene	0·046
2-Methyl-1-propanol	0·050
2-Methyl-2-propanol	0·071
3-Methyl-1-butanol	0·047
2-Methyl-2-butanol	0·067
Cyclohexanol	0·009
Benzyl alcohol	0·019
Isobutyl acetate	0·074
n-Amyl acetate	0·037
Ethyl malonate	0·041
1,1,2,2-Tetrachloroethane	0·014
Acetylacetone	0·039

TABLE II

Values of the adsorption coefficient of hydrogen and of its bulk and surface concentrations

Solvent	$c_{H,bulk}$ mmol l^{-1}	$c_{H,surf}$ mmol g_{cat}^{-1}	K_H l g_{cat}^{-1}
n-Hexane	4·90	2·00	0·408
Cyclohexane	4·09[a]	1·59	0·389
Tetrahydrofuran	3·39	1·68	0·496
Toluene	3·27[a]	1·57	0·480
Ethyl acetate	3·19[a]	1·63	0·511
Ethanol	2·99[a]	1·37	0·458
n-Amyl acetate	1·51	0·69	0·457
Cyclohexanol	0·37	0·20	0·541

[a] Calculated from the Bunsen absorption coefficient values given in ref.[5].

Apparatus and measurement techniques. The solubility of hydrogen in solvents was measured on a standard apparatus for measuring liquid phase hydrogenation kinetics at atmospheric pressure[4]. The procedure was based on the fact that the partial pressure of solvent vapours at the boiling point equals atmospheric pressure. The procedure was as follows: 900 ml of solvent was boiled in a 1 l flask for 10 min to remove dissolved gases and gases in the space above the solvent. The flask then was connected to hydrogen reservoir and thermostatted to 25°C; the reservoir had been thermostatted to that temperature in advance. During the thermostatting, the pressure drop was made up for by adding hydrogen from the reservoir so that the pressure was held constant at the atmospheric pressure value. In addition to the absorption in the solvent, hydrogen was absorbed also in the water replacing the consumed hydrogen in the reservoir; hydrogen also filled the space above the solvent after the cooling down. Conversely, the solvent vapours penetrated into the hydrogen reservoir, until the equilibrium established with the partial pressure equal to the vapour pressure at 25°C over the entire system. After the steady state was attained, the quantity of the consumed hydrogen was determined and the Bunsen absorption coefficient value was calculated (Eq. (*3*)). The measurements for determining the amount of hydrogen adsorbed by the catalyst in the solvent system was analogous; 1 g of catalyst and 10 ml of solvent were used. The adsorbed quantity of hydrogen was calculated according to Eq. (*4*).

RESULTS AND DISCUSSION

Calculation of the Bunsen absorption coefficient. The values of the Bunsen absorption coefficient were calculated from the total consumption of hydrogen (V_H) according to the equation

$$\alpha_S = (273/TV_S)\left[V_H - (V_1 - V_S)(P - P^0)/P + \right.$$
$$\left. + (V_2P^0/P) - (V_H\alpha_{H_2O}T/273)\right], \qquad (3)$$

where the $(V_1 - V_S)(P - P^0)/P$ term represents correction for the filling by hydrogen of the space in the flask above the solvent, the V_2P^0/P term, correction for the penetration of solvent vapours into the hydrogen reservoir, and the $V_H\alpha_{H_2O}T/273$ term, correction for hydrogen absorption in water.

The correctness of the method suggested was verified by comparing the results obtained for methanol and cyclohexane with the published data[5,6]. The agreement was fairly good, the difference did not exceed 5% rel. In these limits lay also the error of measurement as found by repeated experiments. The average α_S values obtained from five replicates are given in Table I.

Advantages of the method suggested are the possibility of employing standard apparatus for kinetic measurements, and work at normal pressure. The results are not so precise as with other techniques, but the precision represented by the relative error of 5% is sufficient for subsequent kinetic measurements.

Calculation of the adsorption coefficient of hydrogen. The surface concentration of hydrogen on the catalyst was determined by using the equation

$$c_{H,surf} = (273/TvW)\left[V_H - (V_1 - V_S)(P - P^0)/P + (V_2P^0/P) - (T/273)(V_H\alpha_{H_2O} - V_S\alpha_S)\right], \qquad (4)$$

where the $V_S\alpha_S$ term represents correction for the solubility of hydrogen in the solvent, the meaning of the remaining terms is the same as in Eq. (*3*).

The average $c_{H,surf}$ values obtained from triplicate measurements are given in Table II along with the K_H values calculated from Eq. (*2*). The various results did not differ from the respective average more than 10% rel. The error involves also a contribution from the small weight (1 g) of the catalyst used.

In spite of the high error of measurement, the adsorption coefficient of hydrogen can be regarded as constant across the solvent series tested, with the value of $K_H = 0{\cdot}47$.

If the assumption of a constant K_H value is extended to all organic solvents used in hydrogenations, the K_H and k values in Eq. (*1*) can really be combined to obtain the relation

$$r = k'c_{H,bulk} \,. \qquad (5)$$

It can be thus summed up that evidence has been gained that the solvent used does not affect substantially the adsorption coefficient of hydrogen which implies that its value in the rate equation for liquid phase catalytic hydrogenation can be included in the rate constant even if the solvents are varied.

LIST OF SYMBOLS

$c_{H,bulk}$	bulk concentration of hydrogen (mol l^{-1})
$c_{H,surf}$	surface concentration of hydrogen (mol g_{cat}^{-1})
k	rate constant (min^{-1})
k'	rate constant including the adsorption coefficient of hydrogen (l min^{-1} g_{cat}^{-1})
K_H	adsorption coefficient of hydrogen (l g_{cat}^{-1})
P	atmospheric pressure (Pa)
P^0	solvent vapour pressure (Pa)
r	reaction rate (mol min^{-1} g_{cat}^{-1})
T	temperature (K)
v	molar volume (ml)
V_H	total hydrogen take up (ml)
V_S	solvent volume (ml)
V_1	volume of the flask up to the cock and the stopper (ml)
V_2	volume of the hydrogen reservoir (ml)
W	weight of the catalyst (g)
α_S	Bunsen coefficient in the solvent used (S) (ml ml^{-1})

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