

DIFFUSION OF GASES IN LIQUIDS. III.*

DIFFUSION COEFFICIENTS

OF HYDROGEN IN ORGANIC SOLVENTS

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Diffusion coefficients of hydrogen, hexane, heptane, octane, benzene, cyclohexane, cyclohexene and acetone were measured at 25°C by the method of dissolving stationary gas bubble in liquid. The obtained experimental values were correlated by multiple linear regression analysis with physical constants of organic solvents and the best correlation relations were obtained with vapour pressure and with solvent viscosity.

In hydrogenation in liquid phase the substrate hydrogenates in large excess of organic solvent and for characterization of the liquid phase are considered physical constants of organic solvent. Diffusion coefficients of hydrogen in organic solvent are not in the literature available¹ and calculation methods based on empirical equations²⁻⁴ provide very inaccurate values. Reaction rate of hydrogenation in the liquid phase is often limited by mass transfer in the catalyst pores (so-called internal diffusion). Study of this phenomena is hindered by the lack of values of diffusion coefficients of reactants in the liquid phase (mostly of dissolved hydrogen). For designing of reactors in the liquid phase is inevitable to measure the value of diffusion coefficients. From a number of methods⁵ has been chosen the method of dissolving a small gas bubble in the gas-free liquid^{1,4,6}. The choice of organic solvents was oriented to solvents currently used in hydrogenation, eventually to prospective solvents for hydrogenation in the liquid phase.

From the obtained diffusion coefficients of hydrogen in organic solvents⁶, a correlation of diffusion coefficients with physical constants of the solvent has been attempted in this work. Successful correlations of diffusion coefficients with vapour pressure and with solvent viscosity have been obtained which, due to number of values and variety of solvent types, can be of general validity.

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EXPERIMENTAL

Chemicals. Electrolytic hydrogen (Technoplyn, Pardubice - Semtín) was purified catalytically at 180°C on the catalyst nickel on kieselguhr (Czechoslovak patent 111 791) and copper on kieselguhr (Czechoslovak patent 91 868). Hexane, heptane, benzene, cyclohexane, acetone (all products of Lachema) analytical grade purity and octane (Laborchemie Apolda DDR) were perfectly dried by sodium and rectified before use. The boiling points were in agreement with tabulated values⁷ with an accuracy $\pm 0.1^\circ\text{C}$. Cyclohexene was prepared on a laboratory unit by dehydration of cyclohexanol on alumina⁸.

Apparatus. The measuring apparatus was described in detail in the previous paper¹. It was supplemented by an automatic recording of expositions (see Fig. 1) consisting of a recorder EZ-3 (Laboratorní přístroje, Prague) and a combination of two-time relays TD-11 (Výzkumný ústav organických syntéz, Pardubice). The time-relays ensured impulses for recording of the time-base. On this time-base were recorded exposition times by connection of the camera with a contact for the flash light. The standard deviation of time measurements was 0.6%. The measuring procedure was the same as in the previous work¹, only exposition times were read off from records of the recorder.

RESULTS AND DISCUSSION

Diffusion coefficients of hydrogen in a series of alcohols and tetrachlormethane¹ were obtained by a graphical evaluation of the time course of dissolving of a small gas bubble in the liquid. Values of diffusion coefficients of hydrogen from previous works^{1,6} have been calculated according to results of solution presented in the previous paper⁹

TABLE I
Experimental Diffusion Coefficients of Hydrogen in Organic Solvents

Liquid	T K	n	$\alpha_0 \cdot 10^2$ ref.	D · 10 ⁵ cm ² /s	A, %
Tetrachloromethane	298	5	7.42 ¹⁰	9.87	5.8
Methanol	293	6	8.40 ¹¹	17.18	4.5
Ethanol	293	6	8.03 ¹¹	14.90	5.8
1-Propanol	298	6	6.85 ¹²	12.84	6.2
2-Methyl-1-propanol	293	6	8.65 ¹¹	7.93	3.9
1-Pentanol	293	5	3.29 ¹¹	16.35	3.1
Hexane	298	6	11.2 ¹⁰	62.38	7.6
Heptane	298	8	10.52 ¹⁰	50.12	11.9
Octane	298	7	9.44 ¹³	44.89	5.55
Benzene	298	6	6.93 ¹¹	20.02	6.90
Cyclohexane	298	7	8.43 ¹⁴	17.32	7.40
Cyclohexene	298	7	7.52 ⁶	22.44	5.68
Acetone	298	3	7.0 ¹¹	41.67	8.10

and are given in Table I. Relatively large standard deviation with heptane was caused by very fast dissolving of gas bubble in the mentioned solvent. In acetone, greater value of standard deviation can be explained by a small number of experiments because some parts of the measuring cell were damaged by acetone during temperation and measurement.

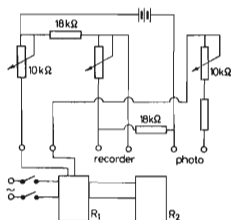


FIG. 1
Schematic View of Time Measuring Device
 R_1 , R_2 Time relays TD-11.

The purpose of correlations of diffusion coefficients with physical constants of the solvent has been to extend the use of measured data on to other organic liquids. The selected physical constants were those used in previously published correlation relations^{3,4,15-17}: molecular weight, density, viscosity, and molar volume of solvent at the boiling point. In this work was also made the correlation of diffusion coefficient with the solvent vapour pressure at the temperature of measurement as suggested in the published paper¹. Values of diffusion factors $F = D \cdot \mu/T$ and physical constants of solvents used in the correlations are given in Table II.

For regression analysis, the organic solvents were divided into three groups: a) alcohols, b) saturated hydrocarbons, c) cyclic hydrocarbons and others. In corre-

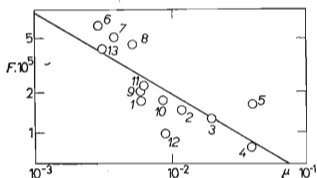


FIG. 2
Correlation Relation (6)

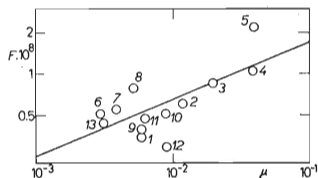


FIG. 3
Correlation Relation (9)

lations were tested diffusion coefficients D and factors F with individual physical constants of the solvents resp. their mutual combinations so that total number of tested correlation relations made was 62. The tested relations were evaluated by multiple linear regression analysis on the digital computer Elliott NCR-4120. Evaluation of individual correlation dependences was done on basis of the t -test by a standard programme of Elliott prepared according to Kendall and Stuart¹⁹.

In Table III are given only correlations for the group of alcohols and for all solvents with physical constants where the significance level determined by the t -test¹⁹ was less than 10%. Correlation relations for hydrocarbons are not given in Table III because of few experimental values in individual homologous series.

From correlations of diffusion coefficient D with individual physical constants of the solvent the only successful was the correlation with viscosity (see Fig. 2). In Table III are also given correlations of diffusion coefficient together with combinations of physical constants: viscosity, solvent vapour pressure at the temperature of measurement (equation (3)), resp. viscosity, solvent vapour pressure at the temperature of measurement, density (equation (10)). The diffusion factor F was correlated in other tests with individual physical constants of the solvent where only the correlations with viscosity were successful (see Fig. (3)) and with solvent vapour pressure at the temperature of measurement (see Fig. 4).

It can be concluded from the presented dependences that if we consider all the measured systems, the dependence of viscosity and of solvent vapour pressure can be used for estimation of other diffusion coefficients. We obtain a more accurate estimate of diffusion coefficients in case of correlation in homologous series of substances. From Fig. 4 can be seen that correlations in a series of alcohols (dashed line) of saturated hydrocarbons (dash and dot line) are fulfilled with substantially higher accuracy. In the series of studied alcohols there is not so well fulfilled the linearity in case of correlation dependence with viscosity (see Fig. 2 and 3) as it is in case of correlation dependence with the solvent vapour pressure (see Fig. 4).

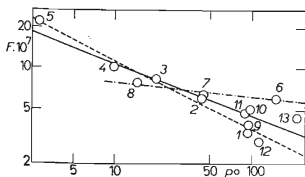


FIG. 4
Correlation Relation (1)

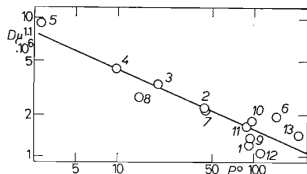


FIG. 5
Correlation Relation (2)

TABLE II
Physical Constants of Solvents Used

Number in Fig.	Solvent	Temperature K	$F \cdot 10^8$ $\text{g} \cdot \text{cm} \cdot \text{s}^{-2} \cdot \text{K}^{-1}$	Vapour pressure ⁷ Torr	Molecular weight ⁷ M g/mol	Density ⁷ ρ g/cm ³	Viscosity ⁷ $\mu \cdot 10^3$ P	Molecular volume ¹⁸ V° cm ³ /mol
1	methanol	293	0.3499	94.15	32.04	0.7915	5.97	42.8
2	ethanol	293	0.6099	43.9	46.07	0.7893	12.00	62.5
3	1-propanol	298	0.8578	20.1	60.09	0.8035	19.92	81.9
4	2-methyl-1-propanol	293	1.0547	9.8	74.12	0.8027	38.99	100.0
5	1-pentanol	293	2.2309	2.8	88.15	0.8184	40.00	121.0
6	hexane	298	0.6151	150.0	86.18	0.6594	2.94	140.7
7	heptane	298	0.6489	45.0	100.20	0.6837	3.86	166.5
8	octane	298	0.7829	14.5	114.23	0.7028	5.20	187.0
9	benzene	298	0.3962	95.0	78.12	0.8787	5.90	96.0
10	cyclohexane	298	0.5112	98.0	84.18	0.7781	8.80	117.0
11	cyclohexene	298	0.4742	89.9	82.14	0.8098	6.30	109.0
12	tetrachloromethane	298	0.2979	114.5	153.84	1.5947	9.00	103.7
13	acetone	298	0.4416	220.0	58.08	0.7908	3.16	77.5

TABLE III
Summary of Correlation Relations

Number of equation	Group	Correlation equation	<i>t</i> -Test (%) significance plane	Relative residual variation	Fig. No
(1)	a, b, c	$\log F = -7.579 - 0.380 \log P^\circ$	0.1	1.38	4
(2)	a, b, c	$\log D \cdot \mu^{1.1} = -4.923 - 0.433 \log P^\circ$	0.1	1.47	5
(3)	a, b, c	$\log D = -5.208 - 0.420 \log P^\circ - 1.08 \log \mu$	0.1	1.47	—
(4)	a	$\log F = -7.437 - 0.502 \log P^\circ$	1.0	1.0	—
(5)	a	$\log F = -11.145 + 1.63 \log V^\circ$	1.0	3.79	—
(6)	a, b, c	$\log D = -4.902 - 0.595 \log \mu$	1.0	4.07	2
(7)	a	$\log F = -10.98 + 1.659 \log M$	1.0	4.08	—
(8)	a, b, c	$\log F = -7.776 - 0.363 \log P^\circ - 0.627 \log \varrho$	5.0	1.0	—
(9)	a, b, c	$\log F = -7.362 + 0.411 \log \mu$	5.0	4.07	3
(10)	a, b, c	$\log D = -5.12 - 0.314 \log P^\circ - 0.732 \log \varrho - 0.921 \log \mu$	10.0	1.08	—

Relation between the diffusion coefficient, vapour pressure and viscosity (equation (3)) was the most favourable of all combined correlations. In this correlations, the value of regression coefficient of viscosity was 1.08 which is a value very close to the exponent in Othmer-Thakar correlation¹⁶ (where it has the value 1.1) where, however, is used the molar volume of solvent instead of vapour pressure.

Fig. 5 illustrates the mentioned regression dependence of the diffusion coefficient, vapour pressure, and viscosity where was used the same value of exponent of viscosity as in the Othmer-Thakar correlation which can be as a certain approximation considered to be the ratio of activation energies of diffusion and viscosity. Correlation by Wilkie and Chang²⁰ proposes as the exponent for molecular weight of the solvent the value 0.5. The obtained regression coefficient had in correlation (7) the value 1.659 so that the correlation dependence with molecular weight was not fulfilled for the studied systems. The same conclusion was made in correlation by Ree, Ree and Eyring²¹ who assumed the exponent with the molar volume to be -0.33. The regression coefficient in correlation (5) was 1.63.

It is necessary to consider the presented correlation relations as empirical dependences that can be very useful in estimating of other diffusion coefficients, since direct measurement of these quantities is rather elaborate.

LIST OF SYMBOLS

D	diffusion coefficient [$\text{cm}^2 \text{s}^{-1}$]
$F = D\mu/T$	diffusion factor [$\text{g cm K}^{-1} \text{s}^{-2}$]
M	molecular weight [g mol^{-1}]
n	number of measurements [—]
P°	vapour pressure [torr]
T	temperature [K]
V°	molar volume [$\text{cm}^3 \text{mol}^{-1}$]
α	Bunsen absorption coefficient [atm^{-1}]
Δ	standard deviation [%]
μ	viscosity [$\text{g cm}^{-1} \text{s}^{-1}$]

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