The hydrodynamics in a simple transport vessel in two-phase systems of organic solvent–water *

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Summary

The hydrodynamics of transport in two-phase systems of organic solvent–water in a very simple apparatus, an unbaffled vessel with an impeller rotating in the center, are discussed. Transport experiments are performed in 3 systems of organic solvent–water at various stirring rates and a constant temperature using various solutes belonging to a congeneric and homologous series of sulfonamides. It is concluded that within a large range of viscosities and stirring rates laminar convective diffusion is an essential feature in this transport process. Equations are presented describing the influence of bulk viscosity and stirring rate on transport rate.

Introduction

Absorption and transport processes of drugs and other xenobiotics into and in a living system influence the physiological or pharmacological effects to a large extent and so the ultimate shape of a quantitative structure–activity relationship (Q.S.A.R.). During these processes at least one membrane has to be passed. Membrane passage is a topic in bioresearch, but the interpretation of the experimental results in this complex process is very difficult. As even the most simple transport process, the one across the interface of two immiscible solvents, is not fully understood, this research is principally the first to be performed.

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* Transport in Q.S.A.R. IX.
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In the literature several apparatuses are described to study interfacial transport. In most experiments the aqueous and organic phases are in some way stirred. Overall transport rate constants for transport from the aqueous to the organic phase and vice versa are determined. However, composition of aqueous and organic phases, experimental set-up, stirring conditions and temperature are not standardized in the literature. This fact makes it difficult to compare the experimental results obtained with the various apparatuses. Augustine and Swarbrick (1970) showed the transport rate constants to be very significantly dependent on the design of the apparatus and the experimental agitation conditions. This must be ascribed to the fact that overall transport rate constants are the result of 3 basic steps: transport in the donor phase to the interface; actual passage of the interface; and transport away from the interface into the acceptor phase. Transport to and from the interface are processes determined by molecular diffusion and convection and of course convection is determined by the experimental agitation conditions. Lewis (1954) already recognized this problem in experiments with two-phase systems and stated that the exact relation between the transfer rates, degree of turbulence and physical properties of the two phases is undoubtedly very complicated and that due to this complexity of the problem no theoretical approach was possible. Just recently some authors tried to describe the hydrodynamics of their experimental apparatus (two-phase systems) and to deduce the contribution of convection and molecular diffusion to their overall transport rate constants (Scholtens, 1977; Byron et al., 1981). However, both theories are not in accordance with each other and are based merely on experiments in one system of organic solvent–water and at one temperature without any experimental proof for these theories to hold for other systems of organic solvent–water. In this paper equations are derived describing the influence of bulk viscosities and stirring rate on transport rate constants, which are shown to hold for various systems of organic solvent–water and which are valid for a wide range of experimental conditions.

Background

De Haan et al. (1983a) presented a theoretical model for the interfacial transfer of a drug, which was proven to hold for 9 systems of organic solvent–water under the applied experimental conditions. In that model k_{aq} and k_{org} are the transport rate constants for transport from the aqueous and the organic bulk, respectively, to the interface and vice versa. The equilibrium at the interface expressed by the partition coefficient P is established instantaneously. This model was shown to be in accordance also with the experimental results obtained by Kubinyi (1977) and Van de Waterbeemd et al. (1981a), who found bilinear relationships between $\log k^{obs}$ (overall transport rate constant) and log P for closely related solutes in a system of organic solvent–water. The general shape of these relationships is reflected by Eqns. 1–4.

$$\log k_i^{obs} = \log P - \log(\beta P + 1) + \log k_{org} \tag{1}$$

$$\log k_2^{obs} = -\log(\beta P + 1) + \log k_{org} \tag{2}$$

$$P = \frac{k_1^{obs}}{k_2^{obs}} = \frac{\text{solute equilibrium concentration in organic phase}}{\text{solute equilibrium concentration in aqueous phase}} \tag{3}$$

$$\beta = \frac{k_{orq}}{k_{aq}} \tag{4}$$

Subscript 1 denotes transport from the aqueous to the organic phase and subscript 2 denotes the reverse process. Van de Waterbeemd et al. (1981b) showed these relationships to hold also for various solutes with a molecular weight varying from 80 to 400 in the system n-octanol–water. This implies k_{aq} (the limit value for k_1^{obs} at high values for P) and k_{org} (the limit value for k_2^{obs} at low values for P) to be solute-independent parameters of a system of organic solvent–water at a constant stirring rate and temperature. This is in agreement with the findings of Lewis (1954). Using dimensional analysis he obtained empirical relationships, which for the transport rate constants in two-phase systems showed a lack of dependence on molecular diffusion coefficients, and he concluded that transport took place by eddy and not by molecular diffusion. However, this conclusion was contradicted by Davies and Rideal (1961), who stated that it is difficult to see how the eddy diffusion could be completely dominant at the moderate stirring rates used in the experimental work.

Lewis (1954) as a starting point still used the classical two-film theory of Whitman, in which it is assumed that both phases are in turbulent motion and that layers exist in each phase immediately adjacent to the interface where the flow is laminar and that diffusion through these layers is slow and rate-determining. Scholtens (1977) and Byron et al. (1981) in their hydrodynamic models for transport in two-phase systems also propose the existence of laminar flow on both sides of the interface. Perry and Chilton (1973) propose the turbulence conditions in the transport vessel to be correlated with the Reynolds number, Re, defined as

$$Re = \frac{S.R. \cdot L^2}{\nu} \tag{5}$$

S.R. is stirring rate (s^{-1}), L is tip-to-tip length of the stirrer blades (m), and ν is the kinematic viscosity ($m^2 \cdot s^{-1}$). For Reynolds numbers between 20 and 10,000 the flow is turbulent at the stirrer and laminar at remote parts of the vessel (Perry and Chilton, 1973). In a previous paper experiments were presented, in which the Reynolds numbers were between 20 and 10,000 (De Haan and Jansen, 1983b). On this basis a laminar flow was assumed to exist on both sides of the actual interface during the performed transport experiments. In the same paper it was shown that substitution of the described laminar flow in the hydrodynamic patterns and corresponding equations given by Grijseels et al. (1981) lead to Eqn. 6 for k_{aq} (the maximum value for k_1^{obs} at high P-values) and a similar expression for k_{org} (the maximum value for k_2^{obs} at low P-values);

$$k_{aq} = X_{aq} \cdot \nu_{aq}^{-5/6} \cdot u^{1/2} \tag{6}$$

Among other factors X_{aq} contains a geometric factor and u is the flow velocity at the interface. It is already indicated that at a constant temperature and stirring rate k_{aq} is a solute-independent parameter and this implies X_{aq} to be a constant for a given system of organic solvent–water. De Haan and Jansen (1983b) already showed k_{aq} and k_{org} to be proportional to $\nu_{aq}^{-5/6}$ and $\nu_{org}^{-5/6}$, respectively, in experiments using one-system organic solvent–water at a constant stirring rate and various temperatures, indicating that laminar flow on both sides of the interface indeed existed. For checking the validity of Eqn. 6 the influence of the stirring rate (S.R.) on k_{aq} and k_{org} also has to be studied. It seems rational to suppose that in our experimental set-up (one stirrer with upper blade in the organic phase and lower blade in the aqueous phase) u is directly proportional to S.R. in a given system of organic solvent–water at a constant temperature. Under these conditions and according to Eqn. 6 plots of $\log k_{aq}$ and $\log k_{org}$ versus log S.R. should give straight lines with a slope of $\frac{1}{2}$ if Eqn. 6 is valid. Another hydrodynamic item of interest is treated by Scholtens (1977) and Byron et al. (1981). According to their hydrodynamic approaches u will be influenced by the bulk viscosities of the aqueous and organic phases. In order to explore possible influences of the bulk viscosities on u in Eqn. 6 experiments are performed in some systems of organic solvent–water with a large spread in viscosities of the organic phases.

Materials and Methods

Materials

In the experiments 4 solvents are used: demineralized water, *n*-hexane (Baker grade), *n*-octanol (Aldrich) and Lytol (Witco). Before use, *n*-octanol is washed with 1 N NaOH, 1 N HCl and water, respectively. *n*-Hexane and Lytol are used as received. Lytol is a hydrogenated petroleum fraction, in which Carbon Atom CN is 19 and Carbon Atom CP is 81 (meaning 19% of all carbon is naphtenic and 81% is paraffinic), which was kindly granted by Witco Chemicals. In all experiments aqueous and organic phases are mutually saturated. Derivatives of N,N-dimethyl-4-[(methyl)amino]benzenesulfonamide are used for solutes in the partition and transport experiments:
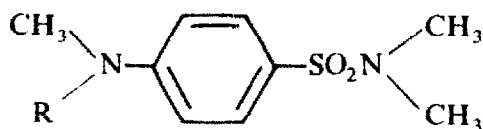
In the experiments with the systems *n*-hexane–water and Lytol–water a homologous series from $R = COCH_3$ up to $R = CO(CH_2)_6 CH_3$ is used; in the experiments with *n*-octanol–water solutes with $R = COCH_2CH_2CONH_2$, $R = COCH_2CH_2OH$ and $R = COCH_2CH_2CN$ are used beside the homologous series from $R = COCH_3$ up to $R = CO(CH_2)_4CH_3$ to obtain the low lipophilicity needed for a reliable

calculation of k_{org}, the limit value for k_2^{obs} at low values for P (see Fig. 1). Syntheses, physicochemical properties and reasons for selection of these model compounds are described by Van de Waterbeemd et al. (1981a).

Apparatus and methods

In all experiments temperature is 20°C with an accuracy of 0.2°C. Values for P and k^{obs} used in the calculations are the mean values of two determinations. Partition coefficients and transport rate constants are determined using the same apparatus and via the same method as described by Van de Waterbeemd et al. (1980). The circulation pump is changed into an MPL E_1 range Metripump and for the stirring at stirring rates 90 rotations per minute (rpm) and 135 rpm (1.50 s^{-1} and 2.25 s^{-1}, respectively) two separate Heidolph stirrers (Type 50111 RZR 1, i = 8 : 1) are used. Transport experiments are performed at 15, 25, 40, 60, 90 and 135 rpm. Kinematic viscosities of aqueous phases saturated with organic solvent (ν_{aq}) and of organic phases saturated with water (ν_{org}) are measured using calibrated Ubbelohde viscosimeters and the presented data are the mean values of 4 determinations.

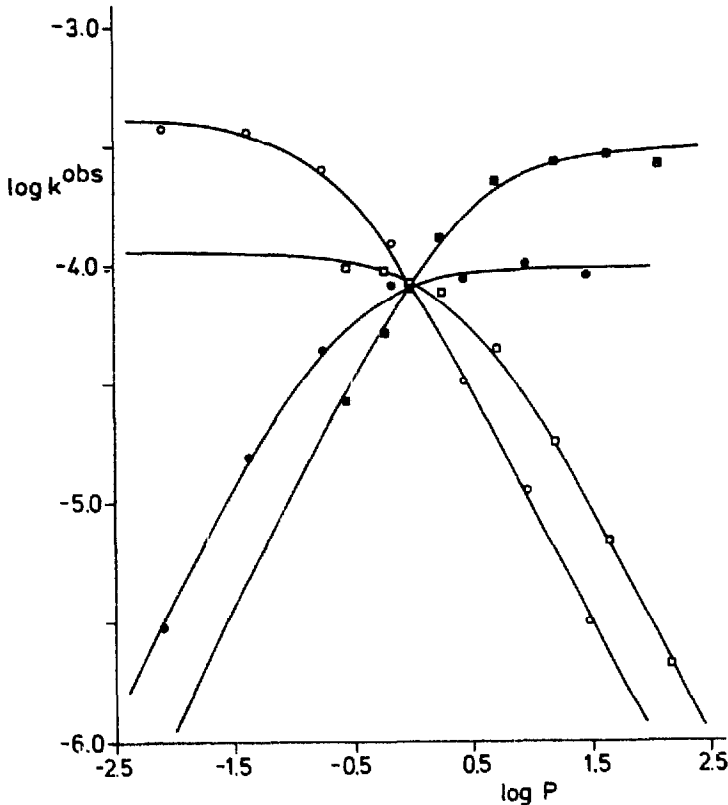Fig. 1. Experimental plots of log k^{obs} vs log P at 20.0°C and 60 rpm. ●, log k_1^{obs} vs log P for n-hexane–water; ■, log k_1^{obs} vs log P for n-octanol–water; ○, log k_2^{obs} vs log P for n-hexane–water; □, log k_2^{obs} vs log P for n-octanol–water.

Results and Discussions

Influence of stirring rate on transport rate constants

It is shown that plots of log k_{aq} and log k_{org} versus log S.R. are expected to give straight lines with a slope of $\frac{1}{2}$. For checking the validity of this assertion and for exploring any possible influence of the bulk viscosities on u in Eqn. 6 (manifested by an influence on k_{aq} and k_{org}) transport experiments are performed at various stirring rates in n-hexane–water ($\nu_{aq} = 1.033 \times 10^{-6}$ m$^2 \cdot$ s^{-1}; $\nu_{org} = 0.473 \times 10^{-6}$ m$^2 \cdot$ s^{-1}) and in n-octanol–water ($\nu_{aq} = 1.003 \times 10^{-6}$ m$^2 \cdot$ s^{-1}; $\nu_{org} = 1.074 \times 10^{-5}$ m$^2 \cdot$ s^{-1}). The theoretical Eqns. 1 and 2 are fitted to the experimental data in the same way as described by Van de Waterbeemd et al. (1981a) and the results are presented in Tables 1 and 2 (Eqns. 7–28). Fig. 1 shows the results at S.R. = 60 rpm (1.00 s^{-1}) and is typical for the results at all mentioned stirring rates.

TABLE 1

RELATIONSHIPS BETWEEN log k^{obs} AND log P IN n-HEXANE–WATER AT 20.0°C AND 5 VARIOUS STIRRING RATES

S.R. (rpm)	relationship	n	r	F	s	Eqn.
15	$\log k_1^{obs} = \log P - \log(3.812\,P + 1) - 3.716$	7	0.999	2168	0.031	(7)
	$\log k_2^{obs} = -\log(3.812\,P + 1) - 3.716$	7	0.999	4079	0.031	(8)
25	$\log k_1^{obs} = \log P - \log(3.801\,P + 1) - 3.614$	7	0.999	2139	0.031	(9)
	$\log k_2^{obs} = -\log(3.800\,P + 1) - 3.614$	7	0.999	4045	0.031	(10)
40	$\log k_1^{obs} = \log P - \log(3.820\,P + 1) - 3.503$	7	0.999	3455	0.024	(11)
	$\log k_2^{obs} = -\log(3.820\,P + 1) - 3.503$	7	1.000	6354	0.024	(12)
60	$\log k_1^{obs} = \log P - \log(4.101\,P + 1) - 3.381$	7	0.999	1728	0.034	(13)
	$\log k_2^{obs} = -\log(4.100\,P + 1) - 3.381$	7	0.999	3441	0.034	(14)
90	$\log k_1^{obs} = \log P - \log(4.134\,P + 1) - 3.288$	7	0.995	542	0.060	(15)
	$\log k_2^{obs} = -\log(4.128\,P + 1) - 3.288$	7	0.998	1102	0.061	(16)

TABLE 2

RELATIONSHIPS BETWEEN log k^{obs} AND log P IN n-OCTANOL–WATER AT 20.0°C AND 6 VARIOUS STIRRING RATES

S.R. (rpm)	relationship	n	r	F	s	Eqn.
15	$\log k_1^{obs} = \log P - \log(0.331\,P + 1) - 4.432$	8	0.999	5027	0.015	(17)
	$\log k_2^{obs} = -\log(0.334\,P + 1) - 4.427$	8	1.000	7251	0.019	(18)
25	$\log k_1^{obs} = \log P - \log(0.361\,P + 1) - 4.206$	8	0.999	2253	0.022	(19)
	$\log k_2^{obs} = -\log(0.361\,P + 1) - 4.206$	8	0.999	5667	0.022	(20)
40	$\log k_1^{obs} = \log P - \log(0.340\,P + 1) - 4.060$	8	0.998	1862	0.025	(21)
	$\log k_2^{obs} = -\log(0.340\,P + 1) - 4.060$	8	0.999	4400	0.025	(22)
60	$\log k_1^{obs} = \log P - \log(0.353\,P + 1) - 3.940$	8	0.998	1231	0.030	(23)
	$\log k_2^{obs} = -\log(0.354\,P + 1) - 3.939$	8	0.999	3130	0.029	(24)
90	$\log k_1^{obs} = \log P - \log(0.361\,P + 1) - 3.820$	8	0.997	966	0.033	(25)
	$\log k_2^{obs} = -\log(0.361\,P + 1) - 3.820$	8	0.999	2486	0.033	(26)
135	$\log k_1^{obs} = \log P - \log(0.375\,P + 1) - 3.683$	8	0.997	856	0.035	(27)
	$\log k_2^{obs} = -\log(0.374\,P + 1) - 3.684$	8	0.999	2320	0.035	(28)

For the aqueous phases in these experiments Re varies from 400 at S.R. = 15 rpm to 3600 at S.R. = 135 rpm. The Reynolds numbers vary from 37 (at 15 rpm) to 335 (at 135 rpm) for the n-octanol phase and from 840 (at 15 rpm) to 5040 (at 90 rpm) for the n-hexane phase. This means that in the performed transport experiments Re is in the range 20 to 10,000, which is indicated above to be one of the demands for the existence of laminar flow on both sides of the interface. From a practical point of view it has to be considered that deviations from Eqn. 6 may occur at low stirring rates due to inhomogeneous mixing of the bulk and at high stirring rates due to droplet formation caused by turbulent flow at the stirrer.

The values for log k_{aq} and log k_{org} are calculated from the experimentally obtained Eqns. 7–28 by using the theoretical Eqns. 1–3 and are presented in Table 3. In Fig. 2 log k_{aq} and log k_{org} are plotted versus log S.R. By linear regression analysis Eqns. 29 and 30 are obtained for the n-hexane–water system and Eqns. 31 and 32 for the n-octanol–water system. These equations represent the drawn lines in Fig. 2.

$$\log k_{aq} = 0.509 \, (\pm 0.022) \log \text{S.R.} \, -4.900 \, (\pm 0.035)$$
$$n = 5 \, (15, 25, 40, 60 \text{ and } 90 \text{ rpm}); \, r = 1.000; \, F = 5439; \, s = 0.004 \tag{29}$$

$$\log k_{org} = 0.561 \, (\pm 0.070) \log \text{S.R.} \, -4.387 \, (\pm 0.113)$$
$$n = 5 \, (15, 25, 40, 60 \text{ and } 90 \text{ rpm}); \, r = 0.998; \, F = 646; \, s = 0.014 \tag{30}$$

$$\log k_{aq} = 0.678 \, (\pm 0.083) \log \text{S.R.} \, -4.697 \, (\pm 0.148)$$
$$n = 5 \, (25, 40, 60, 90 \text{ and } 135 \text{ rpm}); \, r = 0.998; \, F = 679; \, s = 0.015 \tag{31}$$

$$\log k_{org} = 0.708 \, (\pm 0.029) \log \text{S.R.} \, -5.197 \, (\pm 0.053)$$
$$n = 5 \, (25, 40, 60, 90 \text{ and } 135 \text{ rpm}); \, r = 1.000; \, F = 5818; \, s = 0.005 \tag{32}$$

(In these regression equations 95% confidence limits are given in parentheses.)

TABLE 3

LIMIT VALUES log k_{aq} AND log k_{org} FOR n-HEXANE–WATER, n-OCTANOL–WATER AND LYTOL–WATER AT 20.0°C AND VARIOUS STIRRING RATES

Stirring rate (rpm)	n-hexane–water		n-octanol–water		Lytol–water	
	log k_{aq}	log k_{org}	log k_{aq}	log k_{org}	log k_{aq}	log k_{org}
15	−4.297	−3.716	−3.951	−4.430		
25	−4.194	−3.614	−3.764	−4.206		
40	−4.085	−3.503	−3.591	−4.060	−4.055	−4.587
60	−3.994	−3.381	−3.488	−3.939	−3.937	−4.474
90	−3.904	−3.288	−3.378	−3.820	−3.833	−4.344
135			−3.256	−3.683	−3.710	−4.225
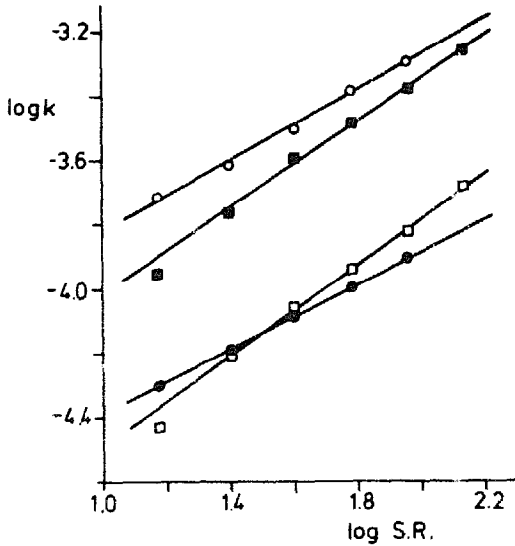
Fig. 2. Experimental plots of log k_{aq} and log k_{org} vs log S.R. at 20.0°C. ●, log k_{aq} vs log S.R. for n-hexane–water; ■, log k_{aq} vs log S.R. for n-octanol–water; ○, log k_{org} vs log S.R. for n-hexane–water; □, log k_{org} vs log S.R. for n-octanol–water.

From Fig. 2 it can be seen that in the experiments in the n-octanol–water system at S.R. = 15 rpm apparently one or both bulk phases is or are not homogeneously mixed, because the corresponding log k-values are relatively too low. Therefore the corresponding data are not taken into account in the linear regression analysis resulting in Eqns. 31 and 32.

The slopes in Eqns. 29–32 may deviate from the expected value of $\frac{1}{2}$ proposed above due to the following phenomenon: in an unbaffled vessel with an impeller rotating in the center centrifugal force acting on the rotating fluid raises the fluid level at the wall of the vessel and lowers the level at the shaft of the impeller. The depth and shape of such a vortex depend on impeller and vessel dimensions as well as rotational speed. Vertical velocities in a vortexing liquid are low relative to circumferential velocities in the vessel (Perry and Chilton, 1973). This vortexing also occurs in the performed transport experiments in two-phase systems and causes an enlargement of the actual interface (= surface available for the transport process). The transport rate parameters k_{aq} and k_{org} are directly proportional to the dimension of this interfacial area. The depth of the vortex (and so the interfacial area) increases at increasing stirring rates and in this way causes the slopes of Eqns. 29–32 to increase (above 0.500).

In the performed experiments the vortex depth in the n-hexane–water system increases from 1.5×10^{-3} m (15 rpm) to 4.0×10^{-3} m (90 rpm) and in the n-octanol–water system from 2.5×10^{-3} m (25 rpm) to 16.0×10^{-3} m (135 rpm). The shape of the vortex is difficult to describe as can be seen in Fig. 3. From this photograph it is evident that it is impossible to calculate the interfacial area exactly. The shape may be approximated to be the segment of a sphere. Using this
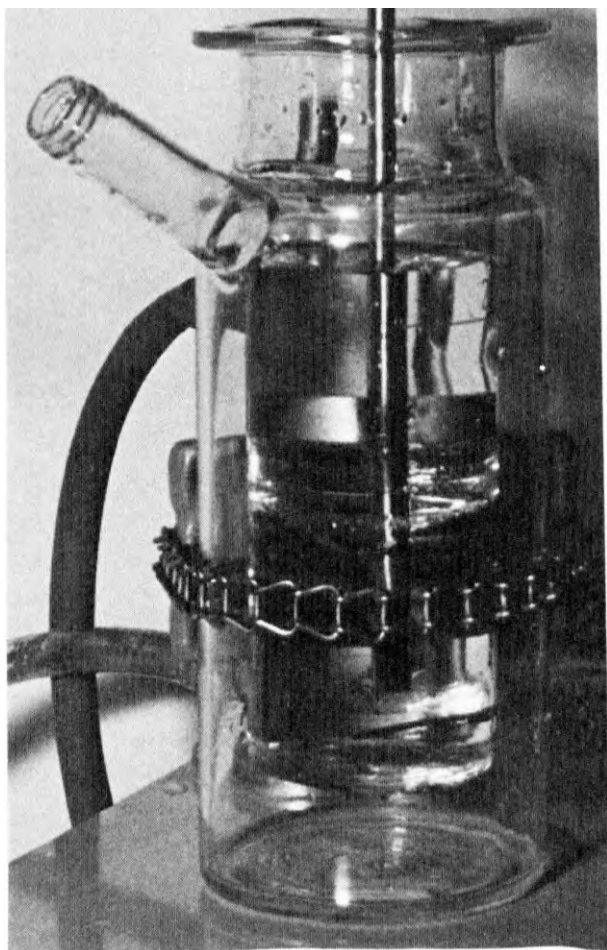
Fig. 3. Photograph of interface between n-octanol and water during transport experiments at 20.0°C and 135 rpm. For the clarity of the photograph the waterjacket for thermostatting is not used. The lid of the transport vessel is omitted in this photograph.

approximation it is calculated that the dimension of the interfacial area in n-hexane–water at 90 rpm is 1.01 times that at 15 rpm. This does not significantly influence the slopes in Eqns. 29 and 30 and indeed the theoretically predicted slope 0.500 is within the 95% confidence limits of the experimentally obtained slopes and it must be concluded that under these conditions k_{aq} and k_{org} are proportional to $(S.R.)^{1/2}$ and so under these conditions Eqn. 6 and its equivalent for k_{org} are valid.

In the same way it is calculated that the dimension of the interfacial area in n-octanol–water at 135 rpm is 1.40 times that at 25 rpm. This enlargement of the interfacial area causes an increase in log k_{aq} and log k_{org} at 135 rpm relative to the values at 25 rpm. This increase amounts to log 1.40 = 0.146. Based on Eqn. 6 the theoretically expected increase in log k_{aq} and log k_{org} for an increase in stirring rate from 25 to 135 rpm amounts to $\frac{1}{2}$(log 135 − log 25) = 0.366. The sum of the calculated increases in log k_{aq} and log k_{org} equals 0.146 + 0.366 = 0.512. On this basis the expected slope for Eqns. 31 and 32 is the quotient of this increase (0.512)

and the corresponding increase in log S.R. (0.732) and amounts to 0.699. This value is within the 95% confidence limits of the slopes of Eqns. 31 and 32. *So when corrections are made for the enlargement of the interfacial area due to vortexing k_{aq} and k_{org} are indeed proportional to (S.R.)$^{1/2}$.*

In general it can be concluded that in our experimental set-up, when corrections are made for the enlargement of the interfacial area, k_{aq} and k_{org} are proportional to (S.R.)$^{1/2}$ for stirring rates between 25 and at least 90 rpm and at least for systems with ν_{org}-values between those of *n*-hexane–water and *n*-octanol–water at a constant temperature. It is already shown that k_{aq} and k_{org} are proportional to $\nu_{aq}^{-5/6}$ and $\nu_{org}^{-5/6}$, respectively (De Haan and Jansen, 1983b). So it must be concluded that Eqn. 6 and its equivalent for k_{org} are valid under the described experimental conditions. *This validity shows diffusion at the interface to be of the laminar convective type.*

Influence of bulk viscosities on u

Despite the fact that the viscosities of both aqueous phases are equal it can be seen in Fig. 2, that k_{aq} for *n*-octanol–water is very significantly higher than for *n*-hexane–water. This is also obvious when the corresponding values for log k_{aq} at 25 rpm (under these conditions the enlargement of the interfacial area in both systems is not more than 1% relative to a totally smooth interface) presented in Table 3 are compared. When the values for log k_{org} + 5/6 log ν_{org} (according to Eqn. 6) at 25 rpm for n-hexane-water and n-octanol-water are compared it is obvious that the value for *n*-octanol–water is again significantly higher than for *n*-hexane–water. According to the discussion in the Background section this could indicate that u is influenced by the bulk viscosities. However, in a previous paper it was concluded that k_{aq} and k_{org} in a system of polar organic solvent–water are larger than in a system of non-polar organic solvent–water (De Haan et al., 1983a). To investigate whether this difference in log k_{aq} and log k_{org} + 5/6 log ν_{org} for both systems has to be ascribed to the difference in bulk viscosities of the organic phases (ν_{org} for *n*-hexane–water and *n*-octanol–water is 0.473×10^{-6} m$^2 \cdot$ s^{-1} and 1.074×10^{-5} m$^2 \cdot$ s^{-1}, respectively), which possibly causes a variation in u of Eqn. 6, or that this difference is due to the chemical structure of the organic phases, transport experiments are performed in Lytol–water ($\nu_{aq} = 1.030 \times 10^{-6}$ m^2 s^{-1}; $\nu_{org} = 6.698 \times 10^{-6}$ m$^2 \cdot$ s^{-1}). Lytol chemically shows a great resemblance to solvents like *n*-hexane and cyclohexane, although its viscosity is closer to that of *n*-octanol. The experimental data are treated in the same way as described for *n*-hexane–water and *n*-octanol–water and the results are presented in Tables 3 and 4 (Eqns. 33–40). The Reynolds number of the aqueous phase varies from 1070 at 40 rpm to 3600 at 135 rpm and of the organic phase from 160 at 40 rpm to 535 at 135 rpm, again within the already discussed range 20–10,000. The vortex depth varies from 4.0×10^{-3} m (40 rpm) to 14.0×10^{-3} m (135 rpm). By linear regression analysis Eqns. 41 and 42 are obtained.

$$\log k_{aq} = 0.647 \, (\pm 0.060) \log S.R. - 5.091 \, (\pm 0.113)$$

$$n = 4 \, (40, 60, 90 \text{ and } 135 \text{ rpm}); \, r = 0.999; \, F = 2137; \, s = 0.006 \tag{41}$$

$$\log k_{org} = 0.691 \, (\pm 0.054) \, \log S.R. \, -5.697 \, (\pm 0.101)$$

$$n = 4 \, (40, 60, 90 \text{ and } 135 \text{ rpm}); \, r = 1.000; \, F = 3068; \, s = 0.005 \tag{42}$$

In the same way as described for n-octanol–water, it is calculated that the dimension of the interfacial area at 135 rpm is about 1.23 times that at 40 rpm. The expected increase in $\log k_{aq}$ and $\log k_{org}$ for experiments from 40 to 135 rpm amounts $\frac{1}{2}\Delta \log$ S.R. (influence of stirring rate based on Eqn. 6) + log 1.23 (enlargement of interfacial area) = $0.664\Delta \log$ S.R. This value 0.664 is within the 95% confidence limits of the slopes of both Eqns. 41 and 42, so again the deviations from 0.500 of the slopes can be ascribed to the enlargement of the interfacial area due to vortexing. The values for $\log k_{aq}$ and $\log k_{org}$ at 40 rpm presented in Table 3 can easily be compared, because in all 3 systems at this stirring rate the enlargement of the interfacial area is smaller than 2% relative to a totally smooth interface. At this stirring rate the value for $\log k_{aq}$ for Lytol–water (-4.055) is very close to that for n-hexane–water (-4.085). In a previous paper $\log k_{aq}$ for the system cyclohexane–water at 40 rpm and 20.0°C ($\nu_{aq} = 1.023 \times 10^{-5} \, m^2 \cdot s^{-1}; \, \nu_{org} = 1.276 \times 10^{-6} \, m^2 \cdot s^{-1}$) is shown to be -4.018 (De Haan et al., 1983a). Considering the chemical composition of Lytol, the value for $\log k_{aq}$ is logically between the $\log k_{aq}$-values for n-hexane–water and cyclohexane–water. This indicates the influence of the organic solvent on k_{aq} to depend on the chemical appearance of the organic solvent and not on its bulk viscosity. Furthermore it has to be noticed that the values for $\log k_{org} + 5/6 \log \nu_{org}$ for n-hexane–water and Lytol–water are very similar but significantly smaller than for n-octanol–water. *So it can be concluded that u in Eqn. 6 and its equivalent for k_{org} is not influenced by the bulk viscosities under the applied experimental conditions.*

Eqn. 6 and its equivalent for k_{org} can now be transformed to Eqns. 43 and 44, which are valid for transport experiments in two-phase systems in an unbaffled vessel with an impeller rotating in the center, when both bulk phases are homogeneously mixed and when no droplet formation due to turbulence at the stirrer and no vortexing take place.

TABLE 4

RELATIONSHIPS BETWEEN $\log k^{obs}$ AND $\log P$ IN LYTOL–WATER AT 20.0°C AND 4 VARIOUS STIRRING RATES

S.R. (rpm)	relationship	n	r	F	s	Eqn.
40	$\log k_1^{obs} = \log P - \log(0.294 \, P + 1) - 4.587$	7	1.000	9385	0.026	(33)
	$\log k_2^{obs} = -\log(0.294 \, P + 1) - 4.587$	7	0.997	802	0.025	(34)
60	$\log k_1^{obs} = \log P - \log(0.291 \, P + 1) - 4.473$	7	1.000	5645	0.033	(35)
	$\log k_2^{obs} = -\log(0.289 \, P + 1) - 4.474$	7	0.994	441	0.034	(36)
90	$\log k_1^{obs} = \log P - \log(0.309 \, P + 1) - 4.344$	7	0.999	5125	0.035	(37)
	$\log k_2^{obs} = -\log(0.308 \, P + 1) - 4.344$	7	0.994	418	0.036	(38)
135	$\log k_1^{obs} = \log P - \log(0.306 \, P + 1) - 4.224$	7	1.000	7165	0.030	(39)
	$\log k_2^{obs} = -\log(0.305 \, P + 1) - 4.225$	7	0.996	607	0.030	(40)

$$k_{aq} = Y_{aq} \cdot \nu_{aq}^{-5/6} \cdot (S.R.)^{1/2} \qquad (43)$$

$$k_{org} = Y_{org} \cdot \nu_{org}^{-5/6} \cdot (S.R.)^{1/2} \qquad (44)$$

Under the discussed experimental conditions Y_{aq} and Y_{org} are constants for a given system organic solvent–water and are influenced by physicochemical properties of the system but not by the bulk viscosities.

Final discussion

Eqns. 30–33, 41 and 42 indicate that under the applied experimental conditions the slopes increase with an increasing value for ν_{org} of the system organic solvent–water. This is caused by an increase of the vortex depth with increasing ν_{org}, while the value for ν_{aq} is almost constant for the 3 systems of organic solvent–water under consideration. Niebergall et al. (1967) and Scholtens (1977) also performed transport experiments in an unbaffled vessel with an impeller (upper blade in the organic phase and lower blade in the aqueous phase) rotating in the center. Niebergall et al. propose k^{obs} to be proportional to $(S.R.)^b$ and Scholtens proposes k_{aq} and k_{org} to be proportional to $(S.R.)^b$. According to them the constant b has to be determined experimentally in the various experimental set-ups. However, as is indicated in this paper, for a good understanding of the obtained values for b all previously discussed eventualities (e.g. vortexing, inhomogeneous mixing of the bulk, droplet formation due to turbulence at the stirrer) have to be considered under the applied experimental conditions. So their empirical values for b (Niebergall et al.: b = 0.70 in *n*-octanol–water at 30°C; Scholtens: b = 0.61 in *n*-butanol–water at 25°C) cannot be compared to our values without due consideration. *However, in general it must be a simple task for a given experimental set-up consisting of an unbaffled vessel with an impeller rotating in the center, to find experimental conditions for which Eqns. 43 and 44 are valid* (e.g. in our case 40 rpm; 20°C; the discussed viscosity range). In that case comparison of experimental results obtained with various apparatuses is very well possible, when the dimension of the interfacial area is known (e.g. in our case 2.04×10^{-3} m²).

The situation for transport experiments in an unbaffled vessel with an impeller rotating in the center now is almost identical to that for the one used nowadays for transport experiments often used rotating diffusion cell (Albery et al., 1976; Albery and Hadgraft, 1979; Guy et al., 1982). In both cases laminar convective diffusion is shown to be an essential feature in the transport process. The equations used for working up the experimental data obtained with the rotating diffusion cell are originally derived for the rotating disc electrode, although the hydrodynamic conditions in both apparatuses are not completely identical (Levich, 1962; Gregory and Riddiford, 1956). Both our Eqns. 43 and 44 and the equations for working up the experimental results obtained with the rotating diffusion cell are experimentally verified to hold for the applied experimental conditions.

So transport experiments can very well be performed in our simple experimental set-up at 40 rpm and 20°C, because under these conditions for at least systems of

organic solvent–water with a value for ν_{org} between those for n-hexane–water and n-octanol–water Eqns. 43 and 44, describing the influence of stirring rate and bulk viscosities on transport rate, are valid.

Conclusion

In transport experiments with two-phase systems of organic solvent–water in an unbaffled vessel with an impeller rotating in the center Eqns. 43 and 44 are valid when both bulk phases are homogeneously mixed and when no droplet formation due to turbulence at the stirrer and no enlargement of the interfacial area due to vortexing take place. The validity of these equations show laminar convective diffusion to be an essential feature in the transport process. Eqns. 43 and 44 (in combination with Eqns. 1–3) describe the influence of stirring rate and bulk viscosities on transport rate constants and can serve as a basis for comparison of experimental results obtained with various comparable apparatus.

It is established that in our experimental set-up Eqns. 43 and 44 are valid in transport experiments at 20°C and at a stirring rate of 40 rpm at least in systems of organic solvent–water with ν_{org} between that of n-hexane–water and n-octanol–water. Under these experimental conditions variations in k_{aq} and k_{org} for the various systems have to be described to variations in Y_{aq} and Y_{org}, which are constants for a given system of organic solvent–water and which are not influenced by both bulk viscosities of the system.

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