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Prediction of interfacial transfer kinetics. I. Relative importance of diffusional resistance in aqueous and organic boundary layers in two-phase transfer cell

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Summary

Interfacial transfer kinetics were determined for 3 series of solute homologues in a variety of aqueous : organic solvent systems in the two-phase transfer cell. Experimentally determined interfacial transfer kinetics were compared to those estimated from a theoretical equation derived by Byron et al. (1981). The importance of aqueous and organic diffusional resistance to solute transfer was examined. A method is described to calculate a theoretical solute and solvent dependent ratio that enables estimation of the dominant diffusional resistance for a particular solute in a given solvent system. Choice of solute and solvent system allowed the predictive theories to be tested under conditions where aqueous, organic or mixed diffusional control predominated. Successful prediction of the transfer kinetics of any homologue in a series was possible in all cases from a knowledge of partition coefficient and transfer kinetics of the parent compound, the partition coefficient of the homologue and some easily determined system variables.

Introduction

In two previous publications we reviewed earlier literature concerned with the study of interfacial transport in a variety of transfer cells and developed a theory

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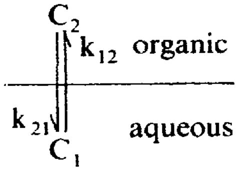


Scheme I

enabling the prediction of non-ionized solute transfer in a symmetrically stirred two-phase transfer cell (Fig. 1) of known dimensions (Byron et al., 1980, 1981). Successful prediction of the apparent first-order rate constant for partitioning, S$(= k_{12} + k_{21}$; Scheme I), of a series of 5,5′-disubstituted barbituric acid derivatives in an octan-1-ol: aqueous system was possible from a knowledge of the transfer kinetics of the lead compound, its partition coefficient, the partition coefficient of the remaining homologues, and some simply determined system-dependent parameters from:

$$S = \left[(D_1 A)/(V_1 h_1)\right]\left\{(K_D + r)/\left[K_D + (R_1)^{-2/3}(R_2)^{1/6}(R_3)^{1/3}\right]\right\} \quad (1)$$

where symbols are defined in the glossary of terms. Eqn. 1 is a simplified form of the original equation (Eqn. 14 in Byron et al., 1981).

Discrimination between compounds on the basis of their partitioning kinetics has been attempted by a number of investigators (Schumacher and Nagwekar, 1974a and b; Augustine and Swarbrick, 1970; Doluisio et al., 1964) in unstandardized transfer cells. These studies provided little insight into the fundamental processes governing solute transfer. It is only recently (Waterbeemd, 1980) that the transport of a wide range of structurally related, non-ionized solutes, has been studied across a number of different aqueous: organic interfaces in a standardized two-phase transfer cell (Fig. 1). Waterbeemd's work has provided insight into the processes that govern

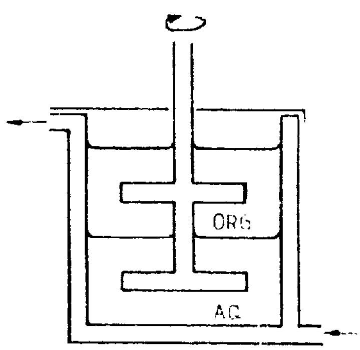


Fig. 1. Two-phase transfer cell. Phase volumes $V_1 = V_2 = 90$ ml in a cell of internal diameter = 6.0 cm. Symmetric stirring employed a 3.7 cm diameter double-bladed paddle positioned 1.4 cm from the interface in each phase.

interfacial transport. In our and Waterbeemd's work, interfacial transfer kinetics are governed by the total diffusional resistance, R_T, at the interface. In the derivation of Eqn. 1, R_T was given by the sum of the resistances of the aqueous and organic diffusive boundary layers adjacent to the interface as:

$$R_T = R_{aq} + R_{org} \tag{2}$$

which by definition (Byron et al., 1980) becomes

$$R_T = \frac{h_1}{D_1} + \frac{h_2}{D_2 K_D} \tag{3}$$

From our earlier work (Byron et al., 1980) the apparent first-order rate constant for partitioning S ($= k_{12} + k_{21}$; Scheme I) is given by:

$$S = \left[\frac{1}{R_T}\right]\left[\frac{A(K_D V_2 + V_1)}{K_D V_1 V_2}\right] \tag{4}$$

which, in the case where $V_1 = V_2 = V$ ($r = 1$) becomes

$$S = \left[\frac{1}{R_T}\right]\left[\frac{A}{V}\right]\left[\frac{K_D + 1}{K_D}\right] \tag{5}$$

Individual values for k_{12} and k_{21} (Scheme I) can then be derived because $S = k_{12} + k_{21}$ and $K_D = k_{12}/k_{21}$ as

$$k_{12} = \left[\frac{1}{R_T}\right]\left[\frac{A}{V}\right] \tag{6}$$

and

$$k_{21} = \left[\frac{1}{R_T}\right]\left[\frac{A}{K_D V}\right] \tag{7}$$

Solving Eqn. 3 for $1/R_T$ and substituting into Eqns. 6 and 7 shows clearly that individual values of k_{12} or k_{21} should rise or fall, respectively, with increasing K_D if the system dependent terms A and V are held constant. Substituting for $1/R_T$ in Eqn. 5, however, reveals that dS/dK_D may be positive negative or zero. Thus, the apparent first-order rate constant for partitioning S($= k_{12} + k_{21}$) may rise, fall or remain constant for a given series as the partition coefficient increases.

In two-phase systems the importance of aqueous and organic diffusional resistances becomes clear on examination of Eqns. 6 and 7 at the two limits as $K_D \rightarrow \infty$ and $K_D \rightarrow 0$. Under these circumstances, $R_T \rightarrow R_{aq}$ and R_{org} (Eqn. 3), respectively,

$(S(=k_{12}+k_{21}) \rightarrow k_{12}$ or $k_{21})$ such that

$$[k_{12}]_{K_D \rightarrow \infty} = \left[\frac{1}{R_{aq}}\right]\left[\frac{A}{V}\right] \tag{8}$$

$$[k_{21}]_{K_D \rightarrow 0} = \left[\frac{1}{R_{org}}\right]\left[\frac{A}{K_D V}\right] = \frac{D_2 A}{h_2 V} \tag{9}$$

Thus at low values for K_D, the resistance of the organic phase should define S and reverse transfer rate constants (Scheme I), while R_{aq} dominates at high values for K_D. Clearly, a knowledge of K_D alone, is insufficient to completely define aqueous or organic diffusional control and therefore we introduce the concept of a resistance ratio, $\gamma = R_{aq}/R_{orq}$, to enable a more complete definition of these terms. For the purpose of this publication therefore, we define 'aqueous diffusional control' as the case where $\gamma \geqslant 20$ ($R_{org} \leqslant 5\%\ R_T$) while organic diffusional control' will be described by $\gamma \leqslant 0.05$ ($R_{aq} \leqslant 5\%\ R_T$). When both diffusional layers are of importance ($0.05 < \gamma < 20$), the system will be said to possess 'mixed diffusional control'.

Prediction of transfer kinetics as a function of K_D (Byron et al., 1981) relied upon introduction of a lead compound from a homologous series into the donor phase of a two-phase transfer cell, in order to monitor C_1 versus time, t. A first-order plot of $\ln(C_1 - C_1^\infty)$ versus t according to

$$\ln(C_1 - C_1^\infty) = \ln(C_1^0 - C_1^\infty) - St \tag{10}$$

provided a value for the apparent first-order rate constant for partitioning, S. The cell constant, $(D_1A)/(V_1h_1)$, could then be calculated by rearranging Eqn. 1 such that

$$(D_1A)/(V_1h_1) = S\left\{\left[K_D + (R_1)^{-2/3}(R_2)^{1/6}(R_3)^{1/3}\right]/(K_D + r)\right\} \tag{11}$$

given values for S, and the previously determined physical constants K_D, r, R_1, R_2 and R_3. Eqn. 1 was then used with $(D_1A)/(V_1h_1)$ = constant, to provide theoretical values for $S(S_{th})$, in close agreement to those determined experimentally for a series of non-ionized 5,5'-disubstituted barbituric acid derivatives in an octan-1-ol : aqueous system. It will be shown later that the transfer of those solutes was subject to, in some cases mixed, but in most cases aqueous diffusional control. In the present publication therefore, solutes and solvent systems have been chosen to test the validity of Eqn. 1 under conditions where organic, aqueous and mixed diffusional control could be expected to dominate.

Experimental

Testing of theory for dependence of transfer kinetics on K_D

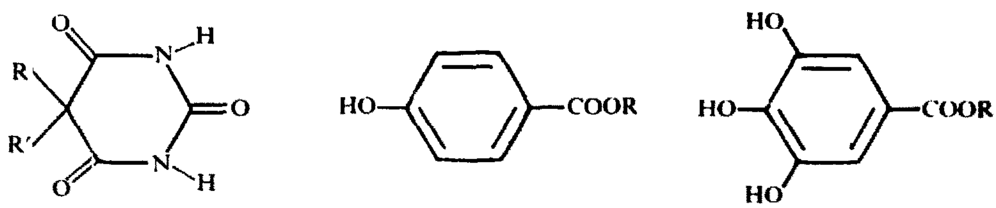
Transfer kinetics were studied for 3 series of non-ionized solutes (A, B and C;

Table 1) in the two-phase transfer cell (Fig. 1) containing equal volumes of aqueous and organic phases according to the method of Byron et al. (1981) with the following modifications. Organic phases were either octan-1-ol, chloroform, or cyclohexane (Spectrograde, Fisons, Loughborough, U.K.) pre-equilibrated with an aqueous phase of 0.3 molal KCl adjusted to pH by the addition of 1 N HCl or NaOH prior to solute introduction. Values for pH were selected to ensure all solutes were insignifi-

TABLE 1

STRUCTURE, pK_a, AQUEOUS PHASE pH, WAVELENGTH EMPLOYED FOR SPECTRAL ANALYSIS, MOLAR ABSORPTIVITY AND SOURCE OF SOLUTES USED IN THE STUDY

SERIES A SERIES B SERIES C



Series	Compound	R	R′	pK_a [a]	pH [b]	Wavelength (nm)	Molar absorptivity [d]	Source
A	I	CH_3CH_2-	CH_3CH_2-	7.88	5.0	222.5	3902	e
	II	CH_2=$CHCH_2$-	CH_2=$CHCH_2$-	7.60	5.0	222.5	5256	f
	III	CH_2=$CHCH_2$-	$(CH_3)_2CH$-	7.81	5.0	222.5	4600	f
	IV	CH_2=$CHCH_2$-	$(CH_3)_2CHCH_2$-	7.66	5.0	222.5	4313	g
	V	CH_2=$CHCH_2$-	$CH_3CH_2CH(CH_3)$-	7.82	5.0	222.5	4659	f
	VI	CH_2=$CHCH_2$-	$CH_3(CH_2)_2CH(CH_3)$-	7.90	5.0	222.5	4538	f
B	I	H-		4.24	2.0	245.0	10859	h
	II	CH_3-		8.22	5.0	267.5	11374	h
	III	CH_3CH_2-		8.28	5.0	267.5	11495	h
	IV	$CH_3(CH_2)_2$-		8.23	5.0	267.5	11702	h
	V	$CH_3(CH_2)_3$-		8.22	5.0	267.5	11911	h
C	I	H-		4.23 [c]	2.0	264.0	7625	h
	II	CH_3-		7.78 [c]	5.0	271.0	9796	i
	III	CH_3CH_2-		7.83 [c]	5.0	271.0	9886	i
	IV	$CH_3(CH_2)_2$-		7.84 [c]	5.0	271.0	10059	h
	V	$CH_3(CH_2)_3$-		7.85 [c]	5.0	271.0	10018	i

[a] Determined by titration at 37 °C, ionic strength = 0.3 molal KCl.
[b] ±0.1.
[c] Forgò et al. (1970).
[d] 37 °C, path length = 1 cm, pH = column 6; Table 1.
[e] Hopkins and Williams, Essex, U.K.
[f] Ganes Chemical Works, Carlstadt, NJ, U.S.A.
[g] Sterling-Winthrop Research Institute, Rensselaer, N.Y., U.S.A.
[h] Sigma Chemicals, St Louis, MO, U.S.A.
[i] Fluka, Chem Fabric, Buchs, Switzerland.

cantly ionized ($<1\%$) and are documented in Table 1. During a transfer experiment pH varied <0.1 pH unit, thereby eliminating the need for buffers in the system. Solutes were introduced into either the aqueous or organic phase in concentrations to produce absorbances in the aqueous phase ranging from 0 to 0.9. Concentrations in the aqueous phase were assayed spectrophotometrically (Model CE 272, Cecil Instruments, Cambridge, U.K.) at wavelengths according to Table 1. All solutes were shown to be stable, and their partition coefficients concentration independent, under the experimental conditions employed during a kinetic run. A stirring speed of 100 ± 0.5 rpm was employed throughout and temperature held constant at $37 \pm 0.1°C$.

Partition coefficients of the solutes and viscosities and densities of the mutually saturated solvents were determined in triplicate at 37°C for all solute–solvent and solvent–solvent systems used in the present study, as described by Byron et al. (1981). Association parameters (ψ) and molecular weight (M) of the pre-equilibrated aqueous and organic phases were assigned values as if they were pure solvents such that $\psi = 2.6$, 1.0, 1.0 and 1.0 for water ($M = 18.02$), octan-1-ol ($M = 130.23$), chloroform ($M = 119.38$) and cyclohexane ($M = 84.16$), respectively. The theoretical dependence of $S(= k_{12} + k_{21})$ on K_D was determined for each system using Eqn. 1, after calculation of an average value for the cell constant $(D_1A)/(V_1h_1)$ for each solute series in each solvent system studied using Eqn. 11 as previously described (Byron et al., 1981). Theoretical values were compared to those experimentally determined from plots of ln(transferable concentration) versus time after linear regression analysis.

Results

Testing of theory for dependence of transfer kinetics on K_D

First-order plots of ln(transferable concentration) versus t were linear for $> 95\%$ of the partitioning process, for each solute studied, in either solvent system, at 100 rpm. Observed terminal slopes, $S_{obs}(= k_{12} + k_{21})$ and partition coefficients, K_D, are documented in Table 2 for series A using 3 different organic phases and series B and C in an aqueous : octan-1-ol system. The terminal slope (S) was determined in each case by linear regression analysis (correlation coefficient $r > 0.999$, $n \geq 10$). Mutually saturated solvent viscosities and densities were determined at 37°C for each solvent pair and are presented in Table 3. Average values for the coefficient $(D_1A)/(V_1h_1)$ for series A using, as the organic phase, octan-1-ol, chloroform or cyclohexane were determined as $6.10\ (\pm 0.25) \times 10^{-2}$, $1.46\ (\pm 0.06) \times 10^{-2}$ and $1.79\ (\pm 0.25) \times 10^{-2}$ min^{-1}, respectively, while series B and C (aqueous: octan-1-ol) provided values of $4.88\ (\pm 0.26) \times 10^{-2}$ and $4.01\ (\pm 0.26) \times 10^{-2}$ min^{-1}, respectively (bracketed terms are standard deviations). The theoretical dependence of S upon K_D for each system studied was evaluated using Eqn. 1 and is presented as S_{th}, alongside the experimental results in Table 2 and Fig. 2. Deviation of theory from experiment was $< 10\%$ for all systems investigated (Table 2).

Discussion

Fig. 2 and Table 2 show the theoretical and experimental dependence of $S(=k_{12} + k_{21}$; Scheme I) on K_D for series A, B and C in a variety of aqueous–organic solvent systems at 100 rpm, 37 °C. There was good agreement between experiment and theory (theoretical prediction of S varies < 10% from empirical determinations,

TABLE 2

ORGANIC/AQUEOUS[a] PHASE PARTITION COEFFICIENTS AND THEORETICAL AND EXPERIMENTAL ESTIMATES FOR $S(=k_{12}+k_{21})$ FOR EACH SOLUTE STUDIED IN THE TRANSFER CELL (100 rpm, 37 °C).

Compound [b]	Organic phase	γ	K_D [c]	S_{th} [d]	S_{obs} [e]	Percent error [f]
AI	Chloroform	1.6	0.82	2.00	2.02	−0.9
AII		5.9	2.98	1.67	1.73	−3.5
AIII		6.9	3.51	1.63	1.51	+7.9
AIV		17	8.35	1.54	1.52	+1.3
AV		20	10.4	1.53	1.48	+3.4
AVI		103	52.2	1.47	1.52	−3.3
AI	Cyclohexane	0.003	0.003	2.04	2.04	0.0
AII		0.008	0.007	2.03	2.14	−5.1
AIII		0.016	0.014	2.03	1.97	+3.0
AIV		0.047	0.041	2.02	2.09	−3.3
AV		0.069	0.061	2.02	1.99	+1.5
AVI		0.25	0.222	1.99	1.89	+5.3
AI	Octanol	1.4	4.8	4.29	4.32	−0.7
AII		4.2	14.4	5.27	4.86	+8.4
AIII		8.4	29.1	5.64	5.81	−2.9
AIV		20	69.6	5.90	6.02	−1.9
AV		25	84.9	5.93	6.16	−3.7
AVI		69	239	6.04	5.92	+2.0
BI	Octanol	8.7	29.9	4.52	4.11	+9.9
BII		23	79.2	4.74	4.79	−1.0
BIII		68	235	4.83	5.03	−3.9
BIV		243	837	4.87	4.98	−2.2
BV		525	1809	4.87	4.95	−1.6
CI	Octanol	0.5	1.64	2.08	2.31	−9.9
CII		1.7	5.69	2.94	2.98	−1.3
CIII		4.7	16.3	3.52	3.36	+4.8
CIV		21	71.9	3.88	3.79	+2.4
CV		70	242	3.97	3.74	+6.1

[a] 0.3 molal KCL adjusted to pH (Table 1).
[b] Table 1; A, B and C indicate compound series.
[c] Observed, mean of 3 determinations.
[d] Eqn. 1; expressed in $min^{-1} \times 10^{-2}$.
[e] $(k_{12}+k_{21})$ based on kinetic analysis; $min^{-1} \times 10^{2}$.
[f] $100\,(S_{th}-S_{obs})/S_{obs}$.

Table 2). Moreover, Fig. 2 shows clearly how transport kinetics may be predicted as a function of partition coefficient given values for the system dependent variables in Eqn. 1.

Table 2 also documents the system and solute dependent variable, $\gamma(=R_{aq}/R_{org})$, as a means of determining whether transport kinetic of a given solute in a specified system is subject to organic, aqueous, or mixed diffusional control. Observing that, in these systems

$$\gamma = (h_1 D_2 K_D)/(h_2 D_1) \tag{12}$$

TABLE 3

MUTUALLY SATURATED SOLVENT VISCOSITIES AND DENSITIES AT 37°C FOR EACH SOLVENT PAIR

Solvent system	η [b]	ρ [c]
Aqueous phase [a]	0.6968	1.0084
octanol	4.4229	0.8194
Aqueous phase [a]	0.7108	1.0070
chloroform	0.4914	1.4562
Aqueous phase [a]	0.6873	1.0080
cyclohexane	0.7042	0.7634

[a] 0.3 molal KCl adjusted to pH (Table 1).
[b] Poise; ($\times 10^2$).
[c] $g \cdot cm^{-3}$.

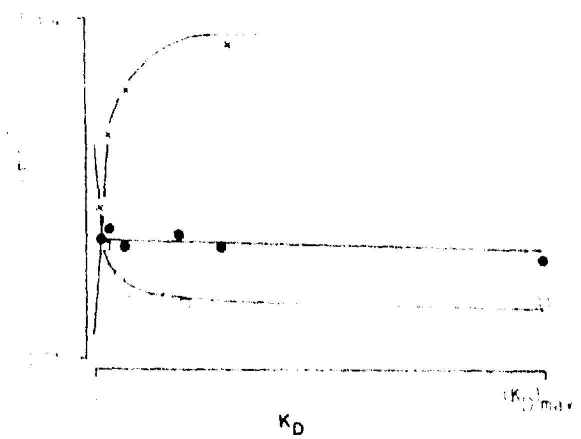


Fig. 2. Theoretical (solid curves; Eqn. 1) and experimental dependence of S on K_D for (×) series C in octanol : aqueous (●) series A in cyclohexane : aqueous and (■) series A in chloroform : aqueous systems at 100 rpm, 37°C. The term $(K_D)_{max}$ is the largest observed partition coefficient for the solute series in the solvent system under investigation (Table 2).

and

$$h_1/h_2 = (R_1)^{-1/3}(R_2)^{-1/6}(R_3)^{1/6} \tag{13}$$

$$D_1/D_2 = (R_1)^{-1}(R_3)^{1/2} \tag{14}$$

(Byron et al., 1981), substituting for h_1/h_2 and D_1/D_2 from Eqns. 13 and 14 in Eqn. 12 and rearranging gives

$$\gamma = (R_1)^{2/3}(R_2)^{-1/6}(R_3)^{-1/3}K_D \tag{15}$$

Eqn. 15 enables calculation of the resistance ratio, γ, from some simply determined system variables.

Values for γ (Table 2), in the two-phase transfer cell, < 0.05, > 20 or in the range 0.05–20 imply organic, aqueous or mixed diffusional control, respectively. Values for γ in Table 2 show cases of organic diffusional, aqueous diffusional and mixed diffusional control. Thus, in this publication, the theory for dependence of S upon K_D (Eqn. 1) has been shown to hold true for systems embracing all forms of diffusional control.

Fig. 2 shows clearly that dS/dK_D can be positive, negative or ~ 0 with increasing K_D, dependent upon the physical properties of the solvent system, confirming our earlier observation based on Eqn. 4. In order to test our theories relating to the change of k_{12} or k_{21}, which should rise and fall, respectively, with increasing values of K_D, theoretical solutions for k_{12} and k_{21} were derived. Since $S = k_{12} + k_{21}$ and $K_D = k_{12}/k_{21}$ substitution into Eqn. 1 gives

$$\begin{aligned} k_{12} &= \left[(D_1A)/(V_1h_1)\right]\left\{K_D/\left[K_D + (R_1)^{-2/3}(R_2)^{1/6}(R_3)^{1/3}\right]\right\} \\ &= \left[(D_1A)/(V_1h_1)\right]\left[1/(1+\gamma^{-1})\right] \end{aligned} \tag{16}$$

and

$$\begin{aligned} k_{21} &= \left[(D_1A)/(V_1h_1)\right]\left\{1/\left[K_D + (R_1)^{-2/3}(R_2)^{1/6}(R_3)^{1/3}\right]\right\} \\ &= \left[(D_1A)/(V_1h_1)\right]\left[1/\left\{K_D(1+\gamma^{-1})\right\}\right] \end{aligned} \tag{17}$$

Fig. 3 shows the agreement between the theoretical (Eqns. 16 and 17) and experimental $[k_{12} = S_{obs}K_D/(K_D+1);\ k_{21} = S_{obs}/(K_D+1)]$ dependence of k_{12} and k_{21} upon γ (directly proportional to K_D, Eqn. 15) for each solvent system studied. For presentation purposes rate constants and γ are expressed in log form. Plots of log k versus log K_D are more frequently used to present this type of data. Because the regions of aqueous, organic and mixed diffusional control are dependent upon the resistance ratio, and not K_D alone, the use of γ as the independent variable in Fig. 3 enables these regions to be displayed in a system-independent fashion. Thus, the abscissa of Fig. 3 shows the 3 distinct regions of diffusional control, described previously, for each solvent system at 100 rpm, 37 °C. The figure clearly demonstrates how k_{12} and k_{21} rise and fall, respectively, independently of the solvent system employed (cf $S(=k_{12}+k_{21})$; Fig. 2) in the study.

In a number of publications, Waterbeemd, (1980, 1983) introduces and emphasizes the importance of the 'ratio of the diffusional rate constants', k_{org}/k_{aq}, $(=\beta)$ in the stagnant diffusive boundary layers adjacent to the interface (Fig. 1, Waterbeemd, 1980) as a cell and solvent-system-dependent constant. His terms, k_{aq}, k_{org} and β are equivalent to $[k_{12}]_{K_D\to\infty}$ (Eqn. 8), $[k_{21}]_{K_D\to 0}$ (Eqn. 9) and γ/K_D, respectively. In a recent publication, Waterbeemd (1983) describes a relationship between β and viscosity based upon the Stokes-Einstein relationship. Work performed in our laboratories (Guest, 1980) has shown that the Stokes-Einstein equation is of limited use for the prediction of diffusion coefficients for low molecular weight solutes in the two-phase transfer cell. Indeed, if this, as opposed to the Wilke-Chang relationship (Wilke and Chang, 1955) is employed to derive our theoretical predictions for tranfer rate constants in this cell, percent errors between theory and experiment can be as high as 60%. In order to describe transfer kinetics for a series of solutes as a function of K_D, Waterbeemd employs 3 distinct equations dependent upon the range of K_D under investigation. His method requires the experimental study of a large number of compounds, in order to derive these, largely empirical, functions. Conversely, our approach describes the variation of transfer kinetics within a series, as a continuous function of K_D according to Eqn. 1 and related Eqns. 16 and 17. The agreement in this paper, between theory and experiment (Figs. 2 and 3) for systems subject to aqueous, organic or mixed diffusional control, attests to the validity of our theories.

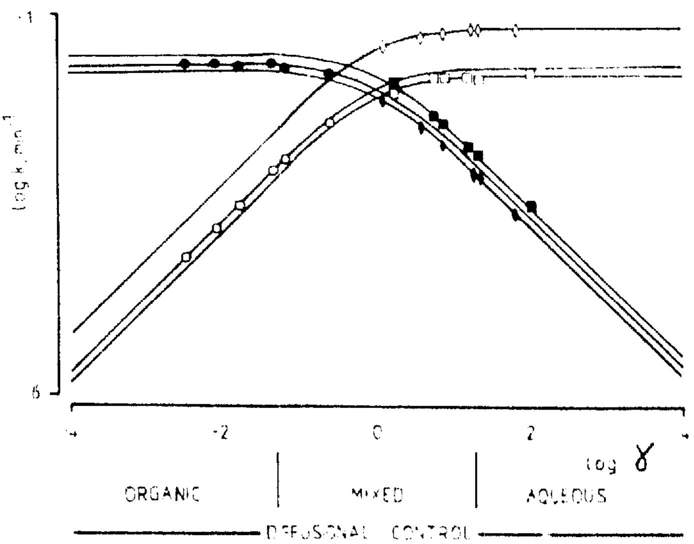


Fig. 3. Theoretical (solid curves; Eqns. 16 and 17) and experimental dependence of the first-order forward, k_{12} (open symbols), and reverse, k_{21} (closed symbols), rate constants for partitioning of solute series A in (◇) octanol: aqueous, (○) cyclohexane: aqueous and (□) chloroform: aqueous systems upon the resistance ratio at 100 rpm, 37 °C.

Application of our theory for prediction of interfacial transfer kinetics (Eqn. 1) necessitates the determination of a cell constant $(D_1A)/(V_1h_1)$ (Eqn. 11). Experimental estimation of $(D_1A)/(V_1h_1)$ for solute series A, B and C in a cyclohexane: aqueous system where $\gamma \leq 0.05$ (organic diffusional control) showed that $(D_1A)/(V_1h_1)$ varied by $< 6\%$ (unpublished observation). In cases where $\gamma \geq 20$, however, (aqueous diffusion control) inter-solute series values for $(D_1A)/(V_1h_1)$ varied by $> 30\%$ indicating a dependence of $(D_1A)/(V_1h_1)$ upon the solute series investigated. Because the term $A/(V_1h_1)$, should remain effectively constant and solute-independent in a chosen solvent system, we propose that experimentally determined values for S are insensitive to intersolute series variation in the aqueous phase diffusion coefficient, D_1, when $\gamma > 0.05$. However, factors known to affect D_1 (Tyrrell, 1961) become of increasing importance as γ increases toward values indicating aqueous diffusion limitation. The effects of aqueous phase ionic strength and ion type upon values for S for these non-ionized, but polar solutes (Table 1) when $\gamma > 20$ will be described in a subsequent publication.

Abbreviations

A	interfacial area
C	concentration
C^0	initial concentration
C^∞	final concentration
D	diffusion coefficient
h	diffusive boundary layer thickness
k_{aq}	diffusion rate constant in aqueous boundary layer (Waterbeemd, 1980)
k_{org}	diffusion rate constant in organic boundary layer (Waterbeemd, 1980)
k_{12}	first-order forward rate constant for partitioning (Scheme 1)
k_{21}	first-order reverse rate constant for partitioning (Scheme 1)
K_D	oil/water partition coefficient
M	molecular weight
r	V_1/V_2
R_1	η_1/η_2
R_2	ν_2/ν_1 (where $\nu = \eta/\rho$)
R_3	ψ_1M_1/ψ_2M_2
R_T	total diffusional resistance
R_{aq}	aqueous diffusional resistance
R_{org}	organic diffusional resistance
S	apparent first-order rate constant for partitioning
t	time
V	volume
β	k_{org}/k_{aq} (Waterbeemd, 1980)
γ	R_{aq}/R_{org}
η	viscosity
ν	kinematic viscosity
ρ	density
ψ	association parameter (Wilke and Chang, 1955)

Subscripts 1 and 2 refer to aqueous and organic phases, respectively. Subscripts th and obs refer to theory and experiment, respectively.

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