

Study of the influence of surfactants on the transfer of gases into liquids by inverse gas chromatography

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Abstract

The experimental technique of the reversed-flow version of inverse gas chromatography was applied for the study of effects of surfactants in reducing air–water exchange rates. The vinyl chloride (VC)–water system was used as a model, which is of great importance in environmental chemistry. Using suitable mathematical analysis, various physicochemical quantities were calculated, among which the most significant are: Partition coefficients of the VC gas between the surfactant interface and the carrier gas nitrogen, as well as between the bulk of the water + surfactant solution and the carrier gas nitrogen, overall mass transfer coefficients of VC in the liquid (water + surfactant) and the gas (nitrogen) phases, water and surfactant film transfer coefficients, nitrogen, water and surfactant phase resistances for the transfer of VC into the water solution, relative resistance of surfactant in the transfer of VC into the bulk of solution, exchange velocity of VC between nitrogen and the liquid solution, and finally the thickness of the surfactant stagnant film in the liquid phase, according to the three phase resistance model. From the variation of the above parameters with the surfactant's concentration, important conclusions concerning the effects of surfactants on the transfer of a gas at the air–liquid interface, as well as to the bulk of the liquid were extracted. An interesting finding of this work was also that by successive addition of surfactant, the critical micelle concentration of surfactant was obtained, after which follows a steady-state for the transfer of the gas into the water body, which could be attributed to the transition from mono- to multi-layer state.

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1. Introduction

The air–water interface is a region of intense gradients that impose interesting constraints on the lives and productivity of microorganisms. Research in this area requires working at scales far smaller than those normally associated with the bulk processes on either side of the interface, and requires new experimental and theoretical approaches.

Surfactant films have long been thought to be a factor in modulating physical transfer processes. The molecular organization of these films is an important factor governing interfacial process. Early work [1,2] focused on the static or “barrier” effect of closed packed layers in retarding interfacial transfer of heat and water vapor. However, the expanded films formed by natural biogenesis surfactants at the air–water interface modulate surface roughness and

near surface hydrodynamically, by introducing viscoelastic modulus [3,4]. Recent laboratory studies in wind-wave flumes have yielded new insights on the inhibiting effects of surfactants on gaseous exchange [5].

In this work, the relatively new technique of reversed-flow gas chromatography (RFGC) has been applied for the study of the effect of surfactants on the transfer of a gas into water, which gives information not only on phase equilibria but also on interface transport across the air–water boundaries under conditions with surfactant films present [6–10].

Reversed-flow gas chromatography consists of reversing the direction of flow of the carrier gas from time to time. If other gases are contained in the carrier gas and their concentration depends on a rate process within a chromatographic column, each flow reversal creates perturbation in the chromatographic elution curve in the form of extra peaks, called “sample peaks”. Then, by repeatedly reversing the flow of the carrier gas, a repeated sampling of this rate process is performed.

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RFGC has been used to determine diffusion coefficients of pure gases and of ternary gas mixtures into pure gases [6,11–13] and gas mixtures [14], mass transfer coefficients on solids and liquids [15,16], solubility and interaction parameters [17], adsorption equilibrium constants [18], Lennard–Jones parameters [19], rate constants, activation parameters and conversions of reactants into products for various surface-catalyzed reactions [20–23], rate constants for sorption process of various gases on bimetallic catalysts [24,25], as well as for the study of the flux of gases across air–water interface [26], and for the mechanism of the interaction of vinyl chloride (VC) with water [27]. In [26,28,29] other advances in physicochemical measurements of the method are described.

In the present work, for the study of the influence of surfactants on the transfer of gases into liquids, the vinyl chloride–water system in the presence of the anionic surfactant FL-70 was selected as model due to the reason that vinyl chloride is related to primary group of toxic chemicals carcinogens [30,31], and the surfactant's FL-70 wetting and penetration rate is enhanced more than that of any other surfactant, because of the center position of its ionic sulfate residue.

2. Experimental

2.1. Materials

The surfactant used was FL-70 from Fischer Scientific, which is an anionic surfactant ($\text{pH} \approx 9.5$) composed of 3.0% oleic acid, 3.0% sodium carbonate, 1.8% Tergitol, 1.4%

tetrasodium EDTA, 1.3% triethanolamine and 1.0% polyethylene glycol, made up in water. The main component of FL-70 is Tergitol, 7-ethyl-2-methyl-4-undecyl sulfate sodium salt.

The analytical model gas was vinyl chloride of 99.99% purity from Matheson Gas Products, while the carrier gas was nitrogen of 99.99% purity from BOC gases.

2.2. Apparatus and procedure

A flow diagram of experimental setup is shown in Fig. 1, the details of which have been described elsewhere [7,8] except for the system which was modified for the periodic flow reversal of the carrier gas with an automatic Shimadzu six-port valve. The computer programming during the whole experiment controlled the flow reversals.

A multi-detector gas chromatograph (Shimadzu GC-14 A) containing flame ionization detector along with other detectors, contained in its oven two sections of length l and l' of a stainless-steel chromatographic column [(50+50) cm \times 5.3 mm i.d.] containing no chromatographic material. A stainless-steel diffusion column, consisted of two sections z and y , was connected perpendicularly at its upper end to the middle of column $l + l'$. Section y , in which water was contained, had a volume $V_G' = 4.52 \text{ cm}^3$, a length of 3 cm, and an internal diameter of 18 mm, whilst section z , which was empty of any chromatographic material, had a volume $V_G = 9.10 \text{ cm}^3$, a length 42 cm, and an internal diameter of 5.3 mm.

The end D_1 of the sampling column $l + l'$ was connected via a six-port automatic Shimadzu valve, working with

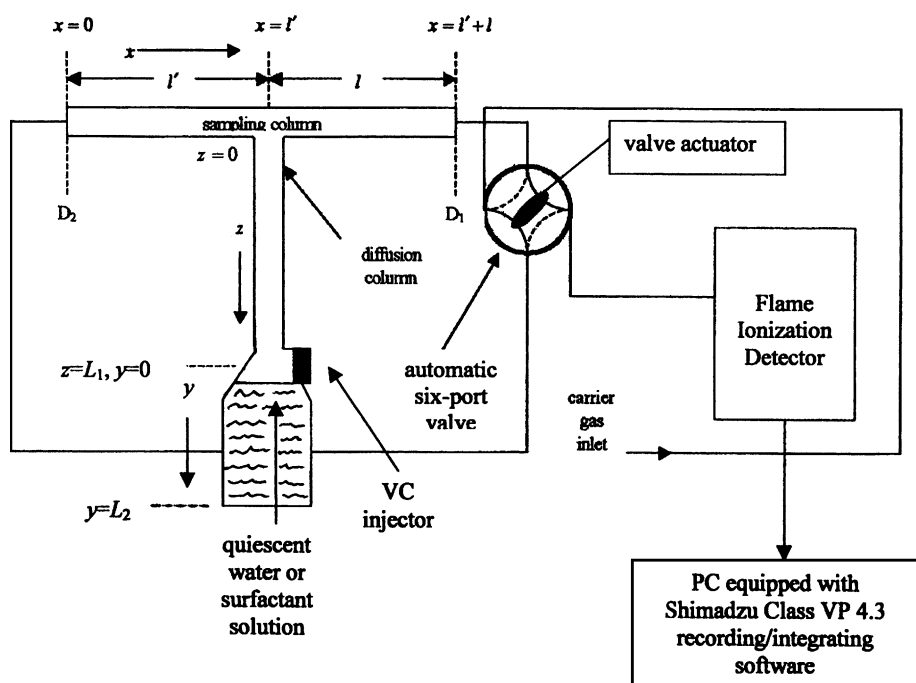


Fig. 1. Schematic representation of the reversed-flow gas chromatographic technique using automatic valve and computer controlled system for studying the effect of surfactants on the interaction of vinyl chloride with water.

programmized system for the periodic flow reversals, to the carrier gas (nitrogen) supply, while the other end D_2 was connected to the flame ionization detection (FID) system. An injector between the two regions z and y permits the introduction of a small gaseous volume (1 cm^3 at atmospheric pressure) of solute (VC).

Through the injector (cf. Fig. 1) 1 cm^3 of vinyl chloride was introduced into the system, at constant temperature and atmospheric pressure. The system was programmized in such a way that as soon as monotonously rising concentration–time curve appears on the computer screen, the chromatographic sampling procedure starts working by reversing the flow of carrier gas through the Shimadzu valve for an exact time period of 6 s. This interval is a shorter time period than the gas hold-up time in both sections of l and l' . As soon as the flow reversals are restored to the original direction of carrier gas by the valve, sample peaks are seen at the PC and thus recorded (Fig. 2), corresponding to various times from the beginning. The programmized procedure operates continuously at various time intervals, during the whole experiment lasting 4 h.

All the experiments were performed at a constant flow rate ($1.0 \text{ cm}^3 \text{ s}^{-1}$) and working temperature 325.2 K , while the pressure drop along $l + l'$ was negligible.

Eight solutions having different percentage volume by volume concentrations: %, v/v ($0.5 < \text{v/v} < 20$) of the anionic surfactant FL-70 in water were used for the study of the influence of surfactants on the transfer of VC into the water body.

3. Results and discussion

It has been shown previously [7,8,32] that the height H of each sample peak (cf. Fig. 2) obtained after reversing the flow of carrier gas for a short time interval is given by the relation:

$$H = 2c(l', t) \quad (1)$$

where $c(l', t)$ is the concentration of the solute (VC) in the sampling column at $x = l'$ and time t (cf. Fig. 1).

The mathematical relations derived, when the lower part L_2 of the diffusion column is empty (cf. Fig. 1), or when it is filled with quiescent pure water or solution of surfactant in water and the distribution equilibrium of analyte gas between the carrier gas and pure water or the surfactant solution is established rapidly, have been described earlier [7,8].

When the distribution equilibrium of VC between the gas and the liquid (pure water or solution of surfactant in water) is established slowly, the diffusion band (after the maximum) is no longer linear, but distorted, as shown previously [7,8]. A new mathematical treatment for the extraction of the relevant equation describing the descending part of this distortion is used [17], which permits the determination of the following parameters.

- (i) Diffusion coefficient of the VC gas into the water body (D_L : $\text{cm}^2 \text{ s}^{-1}$).
- (ii) Partition coefficient of the VC gas between the surfactant interface and the carrier gas nitrogen (K : dimensionless).

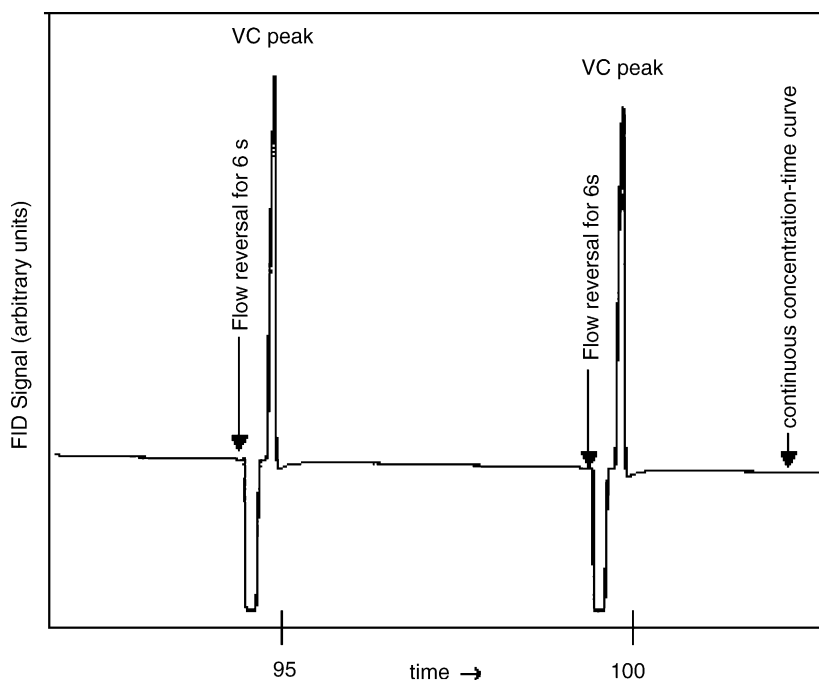


Fig. 2. Reversed-flow gas chromatogram showing two sample peaks for the adsorption of vinyl chloride into water under the influence of the anionic surfactant FL-70 at 325.2 K and 1 atm ($\dot{V} = 1 \text{ cm}^3 \text{ s}^{-1}$).

Table 1

Partition coefficients of VC between the surfactant interface and nitrogen, K , between the bulk of the surfactant solution and nitrogen, K' , as well as between the surfactant interface and the bulk, K'' , Henry's law constants for the dissolution of VC into the surfactant interface, H^+ , diffusion coefficients of VC into the solution, D_L , overall mass transfer coefficients of VC into the surfactant solution, K_L , and nitrogen, K_G , surfactant solution film transfer coefficients of VC, k_L , as well as thicknesses of the surfactant stagnant film in water, z_s , at various percentage volume concentrations of surfactant FL-70 and at 315.2 K

FL-70 in water (% v/v)	K	K'	K''	H^+ (atm)	D_L ($\times 10^4$ cm 2 s $^{-1}$)	ΔD_L^a ($\times 10^4$ cm 2 s $^{-1}$)	K_L ($\times 10^3$ cm s $^{-1}$)	K_G ($\times 10^4$ cm s $^{-1}$)	k_L ($\times 10^4$ cm s $^{-1}$)	z_s ($\times 10^4$ cm)
0.0	12.48	0.40	31.20	128.19	4.33	–	7.50	–	7.57	3.7
0.5	12.99	0.24	54.12	112.52	3.17	1.16	4.52	1.12	4.54	6.98
1.0	13.43	0.31	43.32	108.84	3.57	0.76	4.21	1.31	4.22	8.47
2.0	13.57	0.33	41.12	107.71	3.75	0.58	4.09	1.39	4.10	9.13
3.0	14.00	0.36	38.89	104.41	3.86	0.47	3.97	1.43	3.98	9.70
4.0	14.68	0.38	38.17	99.58	3.95	0.38	3.74	1.44	3.75	10.50
5.0	15.19	0.45	33.75	96.20	4.26	0.07	3.43	1.56	3.44	12.37
10.0	16.31	0.51	32.00	89.59	4.41	–0.08	3.14	1.60	3.16	13.96
20.0	16.53	0.59	27.96	88.41	4.45	–0.12	3.07	1.81	3.08	15.40
Critical ^b (% v/v) FL-70	6.0	5.6	4.8	5.8	5.3	5.6	5.6	4.6	5.5	5.8

1 atm = 101 \times 325 Pa.

^a $\Delta D_L = D_L^{\text{(pure water)}} - D_L^{\text{(surfactant solution)}}$.

^b Value over which the respective quantity remains approximately constant (it was calculated from the cutting point of the two straight lines shown in the figure).

- (iii) Partition coefficient of the VC gas between the bulk of the water + surfactant solution and the carrier gas nitrogen (K' : dimensionless).
- (iv) Partition coefficient of the VC gas between the surfactant interface and the bulk of the water + surfactant solution [$K'' (= K/K')$: dimensionless].
- (v) Henry's law constant for the dissolution of the VC gas into the surfactant interface (H^+ : atm).
- (vi) Overall mass transfer coefficients of VC in the gas nitrogen (K_G : cm s $^{-1}$) and in the liquid solution of surfactant in water (K_L : cm s $^{-1}$).
- (vii) Water (k_w : cm s $^{-1}$) and surfactant (k_s : cm s $^{-1}$) film transfer coefficients for the transfer of VC into the water solution.
- (viii) Nitrogen (r_G : s cm $^{-1}$), water (r_w : s cm $^{-1}$), and surfactant (r_s : s cm $^{-1}$) phase resistances for the transfer of the VC gas into the solution of surfactant in water.
- (ix) Relative resistance of surfactant in the transfer of VC into the bulk of solution (a : dimensionless).
- (x) Exchange velocity (v_e : cm s $^{-1}$) of VC between nitrogen and the solution of surfactant in water.
- (xi) Thickness of the surfactant stagnant film in the liquid phase (z_s : cm).

All these physicochemical quantities and their variation with the %, v/v concentration of surfactant FL-70 in water are presented in Tables 1 and 2 and in Figs. 3–7 (which are representative plots) from which the following conclusions can be drawn.

- (1) The partition coefficients of VC between the surfactant interface and nitrogen, K , as well as between the bulk of the water and surfactant solution and nitrogen, K' , increase with the concentration of surfactant in water, c_s (% v/v), due to increased concentration of VC in both

Table 2

Resistances, r_L , r_w , r_s and r_G , as well as exchange velocities, v_e , for the transfer of VC into water in the presence of the anionic surfactant FL-70 as a function of the percentage volume concentration of surfactant at 315.2 K

FL-70 in water (% v/v)	$r_L = r_w + r_s$ (s cm $^{-1}$)	r_w (s cm $^{-1}$)	r_s (s cm $^{-1}$)	r_G (s cm $^{-1}$)	a^a	v_e ($\times 10^3$ cm s $^{-1}$)
0.0	132.06	132.06	–	–	–	7.520
0.5	220.25	–	88.19	0.55	0.600	4.529
1.0	236.63	–	104.57	0.69	0.559	4.214
2.0	243.63	–	111.57	0.75	0.543	4.092
3.0	251.01	–	118.95	0.80	0.528	3.971
4.0	266.03	–	133.97	0.85	0.498	3.747
5.0	290.33	–	158.27	1.01	0.457	3.432
10.0	316.42	–	184.36	1.13	0.419	3.149
20.0	323.67	–	191.61	1.32	0.410	3.077
Critical ^b (% v/v) FL-70	6.1	–	6.1	5.5	5.7	5.8

^a a is defined by Eq. (5).

^b Value over which the respective quantity remains approximately constant (it was calculated from the cutting point of the two straight lines shown in the figure).

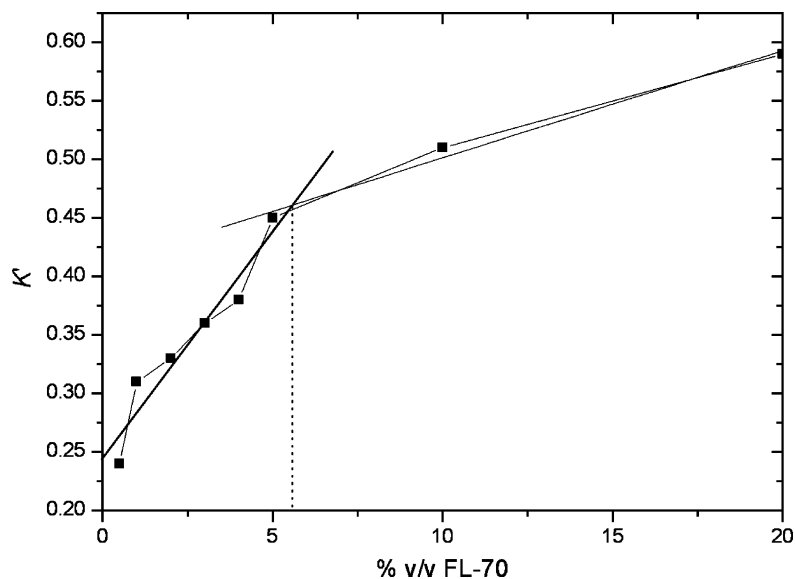


Fig. 3. Variation of partition coefficients of VC between the bulk of the water and surfactant solution and nitrogen (K') with the percentage volume concentration of surfactant FL-70 in water at 325.2 K.

liquid phases in the presence of surfactant. The rhythm of increasing of K' with the anionic surfactant's FL-70 concentration is higher compared to that of K , as the accumulation of FL-70 at the interface hinders the adsorption of VC at the interface. The latter explains also the decrease of the partition coefficient of VC between the surfactant interface and the bulk of the solution of FL-70 in water, K'' , as $K'' = K/K'$. All partition coefficients (K , K' and K'') approach a relatively constant value at surfactant's concentrations approximately higher than 6.0, 5.6 and 4.8% (v/v), respectively (cf. Table 1).

(2) The Henry's law constant, H^+ , for the dissolution of VC at the surfactant interface decreases with the con-

centration of surfactant, as H^+ is inversely proportional to K , which increase with the concentration of FL-70:

$$H^+ = \frac{RTd}{KM_L} \quad (2)$$

where d is the density of the surfactant and M_L its molar mass, and then reaches at a constant value, when the surfactant's concentration becomes higher than 5.8% (v/v).

(3) The diffusion coefficients of VC into the surfactant interface, D_L , increase with the concentration of surfactant in water. Although this is an abnormal behavior, as $D_L \propto K_L$ and K_L decreases with the surfactant's

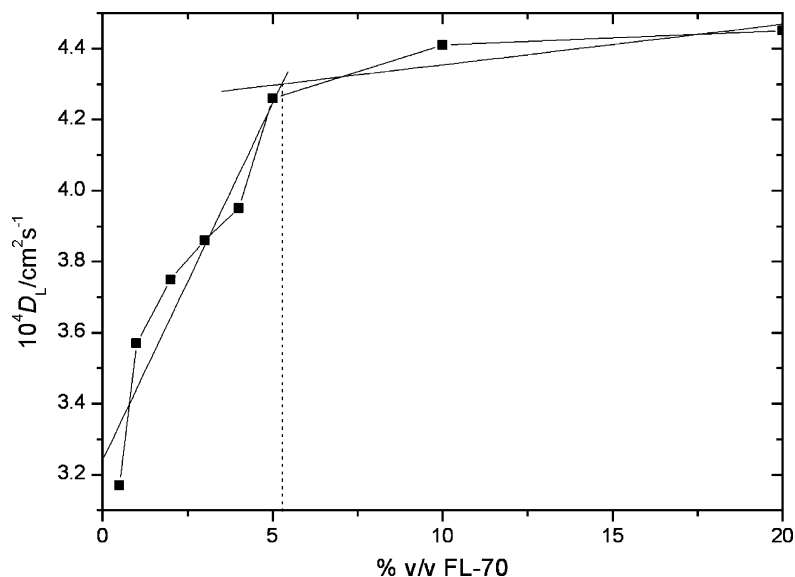


Fig. 4. Variation of diffusion coefficient of VC into the surfactant interface (D_L) with the percentage volume concentration of surfactant FL-70 in water at 325.2 K.

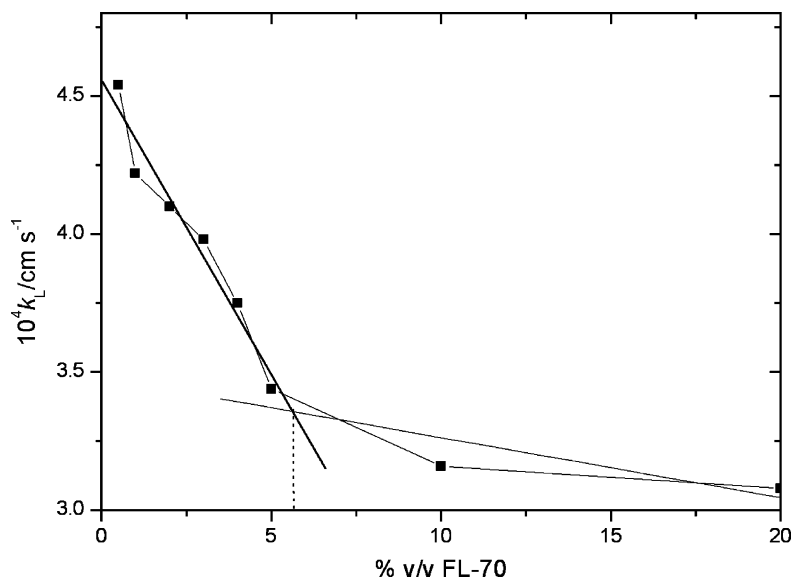


Fig. 5. Variation of liquid film transfer coefficient (k_L) with the concentration of surfactant FL-70 in water at 325.2 K.

concentration, it can be explained on the basis that the differences of D_L for pure water and for the solutions of FL-70 in water, ΔD_L , which account the adsorption of VC at the surfactant interface, decrease with the surfactant concentration c_s , and approach zero at c_s values approximately higher than 5.6%.

- (4) The overall mass transfer coefficients of VC in the liquid (water + surfactant) phase, K_L , decrease with the concentration of surfactant in water. This is due to the fact that surfactant increases the resistance to transfer of the VC gas into the liquid phase and makes the interface rigid. Both these effects increase as the quantity of surfactant in water progressively increase, and, hence,

decrease the liquid phase transfer of the VC gas. The K_L values approach also a constant plateau as the c_s concentration exceeds the value of 5.6% (v/v).

- (5) The overall mass transfer coefficients of VC in the gas (nitrogen) phase, K_G , increase with the surfactant's concentration in water, as $K_G = K' K_L$, and the rhythm of increasing of K' with the surfactant concentration is higher compared to that of decreasing of K_L with c_s .
- (6) The liquid (water + surfactant) film transfer coefficients of VC, k_L , decrease with the concentration of surfactant in water, as k_L is proportional to K_L , until an approximate constant value is obtained, when the surfactant concentration exceeds the value of 5.5% (v/v).

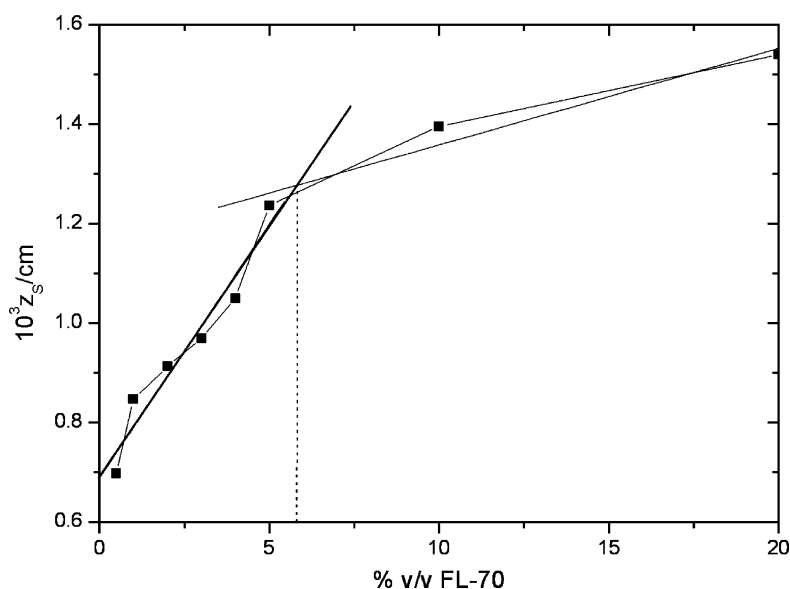


Fig. 6. Variation of thickness of surfactant film in water (z_s) for the transfer of VC into water under the influence of various concentrations of surfactant FL-70 in water at 325.2 K.

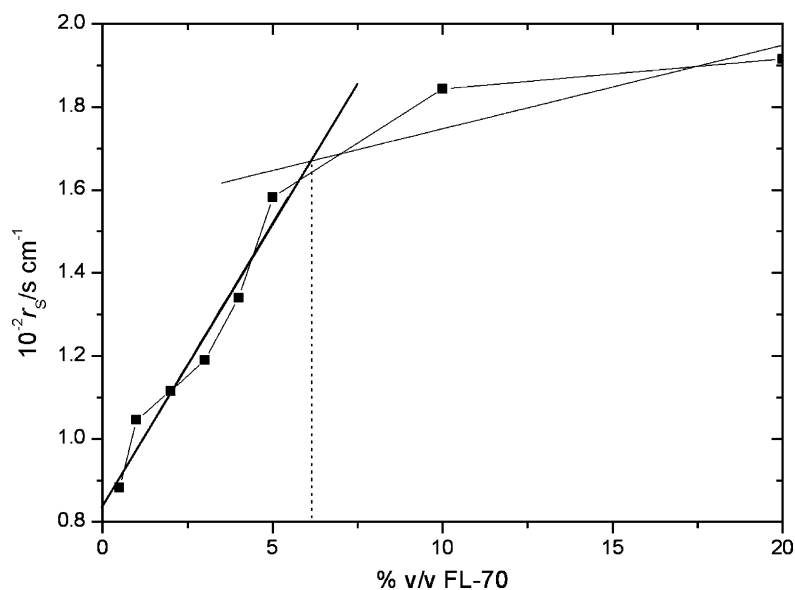


Fig. 7. Surfactant phase resistance (r_s) for the transfer of VC into water under the influence of surfactant's FL-70 concentration at 325.2 K.

- (7) The thickness of the surfactant stagnant film in the liquid phase, z_s , increases with the concentration of surfactant in water, as $z_s = 1/k_L$. This is due to the reason that the surfactant is gathered at the surface of the liquid from the bulk of solution and hence by increasing the concentration of surfactant in water, the liquid film thickness progressively increases and reaches an approximate constant value at concentrations higher than 5.8% (v/v).
- (8) The presence of the surfactant at the gas–liquid interface affects the rate of transfer of the VC solute from the gas to the liquid. The surfactant alters the interfacial region and provides additional resistance to diffusion even when the liquid is quiescent, as it is the case here. In the presence of the anionic surfactant FL-70, the total resistance in the transfer of VC into the water solution, R , is the sum of the resistances in the gas phase, r_G , in the pure water, r_w , and in the surfactant, r_s .

$$R = r_G + r_w + r_s = r_G + r_L \quad (3)$$

where

$$r_L = r_w + r_s \quad (4)$$

The surfactant, r_s , as well as the liquid resistance, r_L , for the transfer of VC into the solution increase with the surfactant's concentration, as $r_L = 1/k_L$, and k_L decreases with c_s . Physically, this means that the transfer of VC into water becomes more difficult at higher concentrations of surfactant, as the liquid (water + surfactant) resistance, which controls this process, increases with surfactant concentration.

- (9) The gas phase resistance of VC, r_G , increases with the concentration of surfactant in water, as $r_G = K'/k_G$ and K' increases with the concentration of surfactant, while the value of k_G is supposed to be constant ($k_G =$

0.4474 cm s^{-1}) [33] and independent of surfactant concentration.

- (10) The ratio of liquid film transfer coefficients of VC with ($k_{L(w+s)}$) and without ($k_{L(w)}$) the surfactant present, a , is the inverse ratio of the corresponding resistances, which accounts the relative resistance of surfactant in the transfer:

$$a = \frac{k_{L(w+s)}}{k_{L(w)}} = \frac{r_G + r_w}{r_G + r_w + r_s} \quad (5)$$

of VC into the water solution body. Parameter a decreases with the surfactant concentration until an approximate constant value is obtained when the surfactant concentration exceeds a critical value (5.7%, v/v), which is characteristic of the surfactant and the gas–liquid system under study.

- (11) The flux of VC between the atmosphere and the water environment depends on the maximum exchange velocity, v_e , which is given by the relation:

$$v_e = \frac{1}{r_G + r_w + r_s} \quad (6)$$

The exchange velocity depends strongly on the surfactant's concentration and decreases with c_s until a critical value of c_s (5.8%, v/v) is obtained after which the v_e value remains approximately constant.

It should be pointed out that it is difficult to estimate the final errors of the physicochemical quantities quoted in Tables 1 and 2, since they come out as a result of a complex series of calculations presented in detail in [7,8], and the application of the rule of error propagation in a long sequence of steps does not give reliable final errors.

It is clear from the results that there is a considerable change in various physicochemical parameters, governing the thermodynamics and kinetics for the transfer of gases

into liquids, when the concentration of surfactant is increased successively. This shows that surfactants play a vital role in the transfer of a gas at the air–water interface.

An important finding of this work is that, there is a critical concentration of surfactant with a mean value of 5.6% (v/v), after which follows a steady-state for the transfer of VC into water (see Tables 1 and 2 and Figs. 3–7). This behaviour can be explained on the ground that the surfactant is present in whole bulk of water but at the same time the molecules of surfactant may make a monolayer on the water surface as well, and with the subsequent concentration of surfactant a stage comes where monolayer is followed by a multi-layer. This stage corresponds to a critical point, as after this we get a steady-state for the transfer of VC into the water body. It means that after this critical point the transfer of VC into water remains constant due to multi-layer formation.

The formation of mono- and multi-layer of surfactant FL-70 at the air–water interface originates from the bulk of the solution. The phenomenon of adsorption at the air–water interface from the bulk solution, which is a slow thermodynamic equilibrium process between the surface and the bulk, with the subsequent formation of monolayer, has been described before [34,35] using various techniques.

In order to give an explanation for the formation of mono- and multi-layer of surfactant FL-70 at the air–water interface, we measured the surface tension of the solutions as a function of the surfactant concentration. Fig. 8 gives the isotherm of surface tension, i.e., the curve which characterizes the change in surface tension of the solution as the concentration of the surfactant FL-70 increases. The isotherm at first sharply drops almost in a straight line as the concentration of the surfactant increases, because at first the liquid (water)–air (nitrogen) interface is free of the surfactant, and almost all small quantities of it present in the solution go to the surface. Then comes a curvilinear

segment of the isotherm which corresponds to the average concentration of the surfactant. Under these conditions, a considerable part of the surface is occupied by the molecules of the surfactant, and this reduces its further adsorption at the interface. Lastly, large concentrations of the surfactant FL-70 (approximately higher than 5.1% (v/v), cf. Fig. 8) are represented by an almost horizontal segment of the isotherm which shows that surface tension depends little on concentration. Under these conditions, a continuous monomolecular layer of the surfactant is formed on the liquid surface and further adsorption is impossible. The later explains our experimental finding that all the measured physicochemical quantities approach a constant value at surfactant's concentrations approximately higher than 5.6% (v/v). At about this stage, further dissolution in the normal way ceases, but now a new process becomes possible. The molecules in the solution begin to aggregate into micelles. This process occurs at a fairly precisely defined concentration, called the critical micellar concentration (cmc) which is the same with the concentration which corresponds to the monolayer formation of the surfactant at the interface (~5.1%, v/v).

3.1. General comparison with literature

- (1) The partition coefficient's K'' values found in the present work, $27.96 < K'' < 54.12$ are in good agreement with those given in literature [36], $12.5 < K'' < 125.0$.
- (2) As it is evident from Table 1, the values of overall mass transfer coefficients K_L , decrease as the concentration of surfactant increases. The same behavior has been observed with a different technique and with different values of mass transfer coefficients [37], in which the K_L values for the transfer of oxygen into water were found to be $7.24 \times 10^{-3} \text{ cm s}^{-1}$ in the absence of surfactant, $7.07 \times 10^{-3} \text{ cm s}^{-1}$ in the presence of the ionic

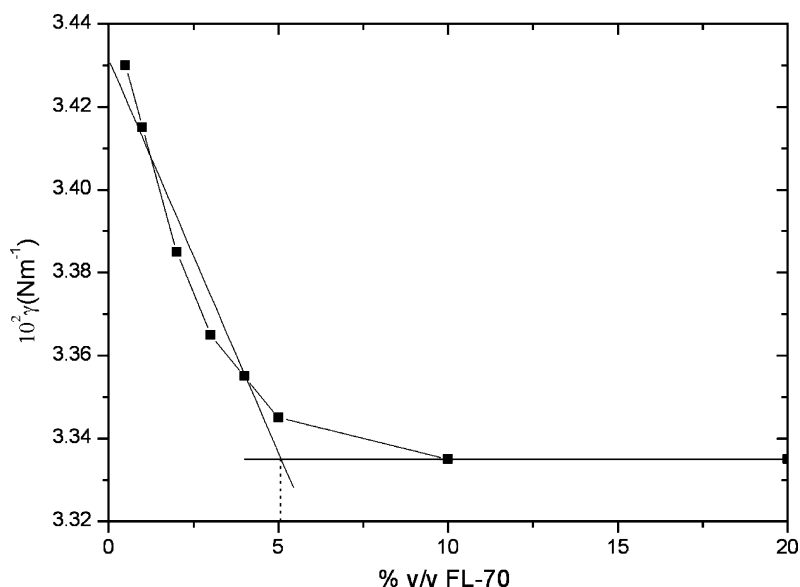


Fig. 8. Surface tension, γ , of the anionic surfactant FL-70 in water as a function of the surfactant concentration (% v/v).

surfactant sodium dodecylbenzene sulphonate (SDS) and $5.96 \times 10^{-3} \text{ cm s}^{-1}$ in the presence of the non-anionic surfactant ethoxylated lauryl alcohol (ELA).

- (3) The film thickness shows a progressive increase with the surfactant's concentration, while the K_L value correspondingly decrease (cf. Table 1). This is also validated by a different technique presented previously [38] in which the K_L is inversely related to film thickness. An illustrative example of decrease in the overall mass transfer coefficients is given in Table 1 of [38], in which the overall mass transfer coefficients from water to air were found to be 0.00 and 0.05 m h^{-1} , when the contaminant concentrations in liquid were 10.00 and 6.88 mol m^{-3} , respectively. This can be attributed to the fact that total amount of the contaminant in the system divided by emission rate, is inversely related to overall mass transfer coefficient. In the same reference it has also been proved with the three-resistance model, that the individual phase or film resistance transfer coefficients vary as a result of modified surfactant concentration at the air–water interface.

4. Conclusions

From the results presented in this work the following conclusions can be drawn.

- (1) The reversed-flow gas chromatography version of inverse gas chromatography can be used with simplicity and accuracy for the study not only of the distribution of a gas between a gaseous and a liquid phase, but also for the effects of surfactants in reducing air–water exchange rates. Using suitable mathematical analysis equations were derived by means of which the relevant physico-chemical quantities describing the thermodynamics and the kinetics of the above processes were calculated.
- (2) As surfactant concentration increases the resistance for transfer of a gas into a liquid increases and makes the interface rigid. Both these effects decrease the transfer of a gas into a liquid phase.
- (3) The thickness of the surfactant stagnant film in the liquid phase, z_s , increases proportionally as the surfactant concentration in the liquid increases.
- (4) Overall mass transfer coefficient, K_L , in the liquid phase is related to thickness of the surfactant stagnant film in the liquid phase inversely, i.e., the more the K_L , the less z_s , and vice versa.
- (5) In all experiments, the surfactant's phase resistance plays a dominant role in the transfer of the VC gas into the liquid solution under the influence of surface-active agents. Hence rate-determining step in adsorption of a gas by water is the transfer of the gas through the surfactant layer, which is an activated process with the permeating gas molecules encountering a potential energy barrier at the surface.

- (6) There is a critical concentration of surfactant called critical micellar concentration between the mono- and multi-layer formation, after which follows a steady-state for the transfer of the gas into the water body.
- (7) The inhibiting effect of surface films on gaseous exchange at gas–liquid interface shows well agreement with literature, in general.
- (8) Results obtained through this work comply with the results given in literature, using the advanced three resistance model than the two-resistance model of Whitman.
- (9) Suggested methodology describes satisfactorily the influences of surfactants on the transfer of vinyl chloride into water as compared with literature and theory and therefore can be extended to other similar environmentally important gas–liquid systems.

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