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MEASUREMENT OF MASS TRANSFER COEFFICIENTS FOR THE EVAPORATION OF LIQUIDS BY REVERSED-FLOW GAS CHROMATOGRAPHY

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SUMMARY

Reversed-flow gas chromatography, a new method for studying heterogeneous catalysis and related phenomena, such as diffusion and adsorption, is applied to the simultaneous determination of mass transfer coefficients for the evaporation of pure liquids or liquid mixtures and the diffusion coefficients of vapours from these liquids into the carrier gas. The necessary mathematical equations were derived and used to calculate the above parameters for the pure liquids methanol, ethanol and propan-1-ol, as well as for the mixtures methanol–water, ethanol–water and propan-1-ol–water, evaporating into carrier gas helium. In the case of mixtures, the variation of the mass transfer coefficient for the evaporation of alcohols with their mole fraction, the working temperature and the carrier gas flow-rate was studied.

The mass transfer coefficients measured depend not only on the nature of the alcohol and the other component in the mixture, but also on the mole fraction. Moreover, they increase with increasing temperature, but they are independent of the carrier gas flow-rate. The values of diffusion coefficients found are in good agreement with those calculated theoretically.

INTRODUCTION

In a recent publication[1] we reported a gas chromatographic (GC) method for measuring mass transfer coefficients for evaporation of pure liquids and diffusion coefficients of vapours into the carrier gas. The method, called reversed-flow gas chromatography (RFGC), is based on a perturbation imposed on the carrier gas flow by reversing its direction from time to time. When the carrier gas contains other gases at certain concentrations, recorded by the detector system, the flow reversals create perturbations on the chromatographic elution curve, with the form of extra peaks ("sample peaks"). If the concentration of a constituent in the flowing gas depends on a rate process, taking place within the chromatographic column, then, by repeatedly reversing the flow, one performs a repeated sampling of this rate process, *e.g.* of the slow diffusion of the constituent vapour into the carrier gas. Using suitable mathematical analysis, equations are derived by means of which the rate coefficient of the slow process responsible for the sample peaks is determined.

RFGC has been used to determine gas diffusion coefficients in binary and

ternary mixtures[2-4], adsorption equilibrium constants[5], molecular diameters and critical volumes in gases[6], Lennard-Jones parameters[7], activity coefficients[8], mass transfer coefficients on solid adsorbents[9], rates of drying of catalysts[10], and rate constants, activation parameters, as well as catalytic conversions of the reactants into products for various important surface-catalysed reactions[11-18]. The method has recently been reviewed[19].

In the present paper the method outlined above is extended to the determination of mass transfer coefficients for evaporation of liquid mixtures, together with the diffusion coefficients of their vapours into the carrier gas.

EXPERIMENTAL

The solutes used were Merck "uvasol" (methanol) and "pro analysi" (ethanol, propan-1-ol). The carrier gas was helium of 99.99% purity from Linde (Athens, Greece).

The apparatus used and the experimental procedure followed have been described elsewhere[1,8]. A conventional gas chromatograph (Pye Unicam, Series 104) with a flame ionization detector contained in its oven two sections l' and l of a stainless-steel chromatographic column (100 + 100 cm × 4 mm I.D.), empty of any solid material, as Fig. 1 shows. The ends of this column D_1 and D_2 were connected to the carrier gas supply and the detector via a six-port valve. A stainless steel diffusion column of length L (112.8 cm × 4 mm I.D.) was connected perpendicularly
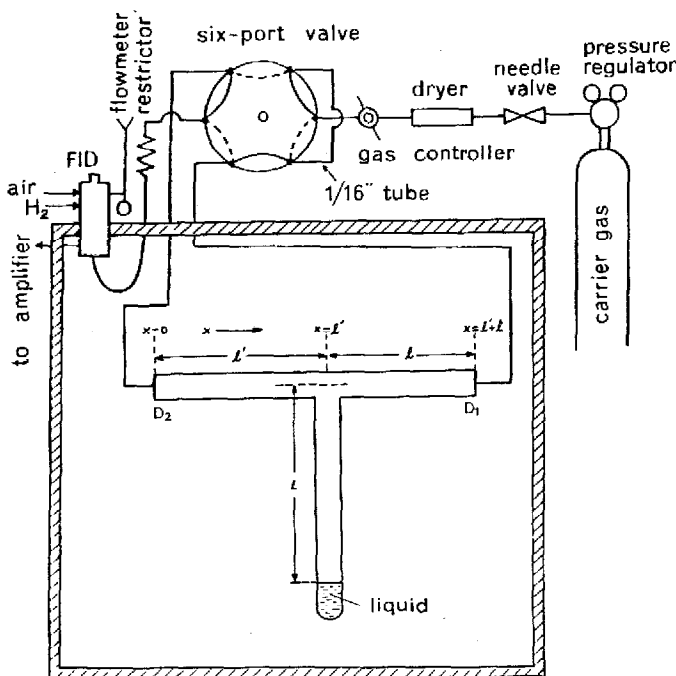

Fig. 1. Experimental set-up for measuring mass transfer coefficients for the evaporation of liquids by reversed-flow gas chromatography.

TABLE I

MASS TRANSFER COEFFICIENTS FOR THE EVAPORATION OF THE ALCOHOL COMPO-
NENT AT VARIOUS MOLE FRACTIONS X_A FROM ALCOHOL–WATER MIXTURES, AND DIF-
FUSION COEFFICIENTS OF THE ALCOHOL VAPOUR INTO HELIUM AT 1 atm PRESSURE

Alcohol	$T(K)$	$\dot{V}(cm^3\ s^{-1})$	$10^2 X_A$	$10^4 k_c\ (cm\ s^{-1})$	$10^3 D\ (cm^2\ s^{-1})$		
					This work	Calc.	Accuracy (%)
Methanol	323.5	0.607	2.3	134	683	688	0.7
			4.7	204	688	688	0
			10.0	239	737	688	6.7
			30.8	254	718	688	4.2
			64.0	261	708	688	2.8
			100.0	339	688	688	0
Ethanol	335.9	0.611	1.6	127	569	590	3.7
			3.3	167	605	590	2.5
			7.2	227	593	590	0.5
			24.0	266	607	590	2.8
			100.0	278	610	590	3.3
Propan-1-ol	342.4	0.681	0.49	117	470	467	0.6
			0.99	143	499	467	6.4
			2.6	174	512	467	8.8
			5.7	220	486	467	3.9
			7.4	229	480	467	2.7
			26.5	238	449	467	4.0
			48.9	264	472	467	1.1
			100.0	292	480	467	2.7

at its upper end to the middle of the column $l' + l$. At the lower end of column L a 2-cm tube containing 0.5 cm³ of a pure liquid or a liquid mixture was connected by means of a 0.25 in. union.

A certain time after the liquid is placed in position, during which no signal is noted, an ascending concentration–time curve for the vapour of the pure liquid or the liquid mixture is recorded, rising continuously and approaching a limiting pla-teau. During this period the direction of the carrier gas flow is reversed for a time period shorter than the gas hold-up time in both column sections l' and l, and then is restored to the original direction. After a certain dead time, an extra signal (sample peak) is recorded (cf. Fig. 3 of ref. 1, and Fig. 2 of ref. 8). The reversal of the flow is repeated several times, always with the same duration (12 s) of backward flow. This gives rise to a series of peaks corresponding to various times t_0 from the begin-ning.

The pressure drop along column $l' + l$ was negligible. The working tempera-ture was in the range 298–347 K, and the volumetric carrier gas flow-rate $\dot{V}$ (corrected at column temperature) was in the range 0.250–0.957 cm³ s⁻¹.

RESULTS AND DISCUSSION

It has been shown[1] that each sample peak produced by a short flow reversal is symmetrical and its maximum height h from the ending baseline is given by

$$h \approx 2c(l', t_0) = \frac{2k_c D c_0}{v(k_c L + D)}\{1 - \exp[-2(k_c L + D)t_0/L^2]\} \qquad (1)$$

TABLE II

MASS TRANSFER COEFFICIENTS FOR THE EVAPORATION OF THE ALCOHOL COMPONENT FROM ALCOHOL–WATER MIXTURES AT CONSTANT ALCOHOL MOLE FRACTION AND VARIOUS TEMPERATURES, ENERGIES OF ACTIVATION, E_a, FOR THE EVAPORATION PROCESS, AND DIFFUSION COEFFICIENTS OF THE ALCOHOL VAPOUR INTO HELIUM AT 1 atm PRESSURE

Alcohol	$10^2 X_A$	$\dot{V}$ (cm³ s⁻¹)	T (K)	$10^4 k_c$ (cm s⁻¹)	E_a (kJ mol⁻¹)	$10^3 D$ (cm² s⁻¹) This work	Calc.	Accuracy (%)
Methanol	10.0	0.598	303.2	99	31.0	607	617	1.6
			312.9	134		624	654	4.8
			323.5	239		737	608	6.6
			324.2	227		674	694	3.0
			328.1	236		672	712	6.0
			333.5	288		721	729	1.1
Methanol	30.8	0.598	298.0	169	12.9	464	598	28.9
			312.6	228		537	650	21.0
			323.5	254		718	688	4.2
			329.0	279		747	713	4.6
			334.5	304		742	734	1.1
Ethanol	7.2	0.601	316.3	149	20.2	527	533	1.1
			326.0	171		546	561	2.7
			330.8	215		572	575	0.5
			335.9	227		593	590	0.5
			344.6	274		615	616	0.2
Propan-1-ol	5.7	0.632	322.7	118	35.3	400	421	5.3
			330.2	152		441	438	0.7
			336.0	246		473	452	4.4
			342.4	220		486	467	3.9
			347.2	312		556	478	14.0

where $c(l', t_0)$ is the vapour concentration at $x = l'$ (*cf.* Fig. 1), the time t_0 is measured from the moment of placing the liquid at the bottom of column L to the last backward reversal of gas flow, k_c is the mass transfer coefficient for solute evaporation, D is the diffusion coefficient of the solute vapour into the carrier gas, c_0 is the concentration of the vapour in equilibrium with the bulk liquid phase at the working temperature, and v is the linear velocity of the carrier gas.

Modification of eqn. 1 leads to two approximate solutions, one for short and one for long times[1]. The latter approximation is

$$\ln(h_\infty - h) = \ln h_\infty - [2(k_cL + D)/L^2] t_0 \qquad (2)$$

where h_∞ is the infinity value for the peak height, given by the expression in front of the braces $\{\ \}$ of eqn. 1, *i.e.* $2k_cDc_0/[v(k_cL + D)]$. Eqn. 2 shows that a plot of $\ln(h_\infty - h)$ *versus* t_0 should be linear, and from the slope $-2(k_cL + D)/L^2$ a first-approximation value for k_c can be calculated from the known value of L and a theoretically calculated value of D. This value of k_c can be used to plot the data at short times according to the short-time approximation, which is[1]

$$\ln\left[h\left(\frac{L}{2t_0^{1/2}} + k_c t_0^{1/2}\right)\right] = \ln\left[\frac{4k_c c_0}{v}\left(\frac{D}{\pi}\right)^{1/2}\right] - \frac{L^2}{4D} \cdot \frac{1}{t_0} \qquad (3)$$

From the slope $-L^2/4D$ of a plot of the left-hand side of eqn. 3 *versus* $1/t_0$, a first experimental value for D is found. This can be used with the slope found from the plot of eqn. 2 to calculate a better approximation of the k_c value, and this in turn is used to replot eqn. 3 for a better approximation of the D value. These iterations can be continued until no significant changes in the values of k_c and D result, but it is not usually necessary to go beyond the first iteration.

The mass transfer coefficients k_c for the evaporation of pure liquids (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, methanol, ethanol, propan-1-ol, butan-1-ol, and pen-
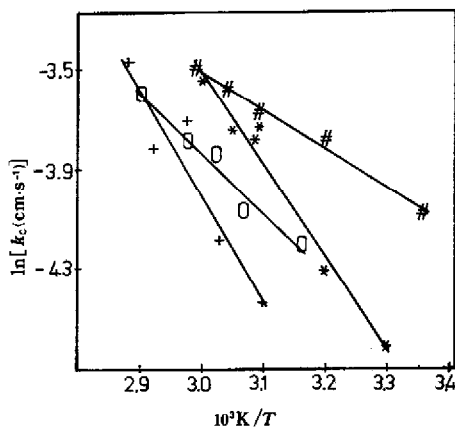

Fig. 2. Temperature dependence of k_c for the evaporation of the alcohol from the following alcohol–water mixtures: $*$ = methanol–water (X_A = 0.100); $\#$ = methanol–water (X_A = 0.308); $\bigcirc$ = ethanol–water (X_A = 0.072); $+$ = propan-1-ol–water (X_A = 0.057).

tan-1-ol) were reported previously[1]. In the present paper the coefficients for the evaporation of the liquid mixtures methanol–water, ethanol–water, and propan-1-ol–water, as well as the diffusion coefficients of the alcohol vapours into the carrier gas helium, were determined.

Table I summarizes the results obtained with all the liquid mixtures studied at one temperature and various alcohol mole fractions. Comparison of the diffusion coefficients found with those calculated theoretically, using the Hirschfelder–Bird–Spotz equation[20], permits the calculation of the method's accuracy, which is defined as

$$\text{Accuracy (\%)} = \frac{|D_{\text{found}} - D_{\text{calc}}|}{D_{\text{found}}} \cdot 100 \tag{4}$$

This is given in the last column of Table I.

The table shows that the k_c values increase with increasing alcohol mole fraction X_A. In all cases there is a steep rise in k_c and then a levelling off with increasing mole fraction. This levelling begins when the alcohol mole fraction becomes larger than *ca.* 0.1, showing that the alcohol–water mixtures with a larger mole fraction behave similarly to the pure alcohols during evaporation.

Mass transfer coefficients for the evaporation of the alcohol component at a constant mole fraction and various temperatures, diffusion coefficients of the alcohol vapour into helium at these temperatures, and the activation energies E_a for the evaporation process, are compiled in Table II. Two conclusions can be drawn from this Table. First, that the k_c values increase with increasing temperature in accordance

TABLE III

MASS TRANSFER COEFFICIENTS FOR THE EVAPORATION OF THE ALCOHOL COMPONENT FROM ALCOHOL–WATER MIXTURES AT CONSTANT TEMPERATURE AND MOLE FRACTION, BUT VARIOUS CARRIER GAS FLOW-RATES; ALSO, DIFFUSION COEFFICIENTS OF THE ALCOHOL VAPOUR INTO HELIUM AT 1 atm PRESSURE

Alcohol	$T(K)$	$10^2 X_A$	$\dot{V}(cm^3\ s^{-1})$	$10^4 k_c\ (cm\ s^{-1})$	$10^3 D\ (cm^2\ s^{-1})$		
					This work	*Calc.*	*Accuracy (%)*
Methanol	324.2	10.0	0.286	217	680	688	1.2
			0.408	222	698	688	1.4
			0.598	227	674	688	2.1
			0.812	225	682	688	0.9
			0.925	218	676	688	1.8
Ethanol	335.9	7.2	0.250	195	536	590	10.0
			0.398	230	572	590	3.1
			0.601	227	593	590	0.5
			0.746	227	583	590	1.2
			0.939	231	559	590	5.5
Propan-1-ol	342.4	5.7	0.278	217	483	467	3.3
			0.439	216	532	467	12.2
			0.632	220	486	467	3.9
			0.822	216	508	467	8.0
			0.957	212	464	467	0.6

with the Arrhenius equation (*cf.* Fig. 2); this is to be expected, since the k_c values are rate coefficients for evaporation. Second, that the activation energy for the evaporation of the same alcohol (methanol) depends strongly on its mole fraction. All E_a values, as expected, are smaller than 40 kJ mol^{-1}, since the evaporation is a physical phenomenon.

Table III lists the values of k_c and D found at constant temperature and alcohol mole fraction, but with various carrier gas flow-rates. As expected, both these parameters are independent of the flow-rate, since k_c is a rate coefficient and the D values of Table III are all referred to 1 atm pressure. The fact that the k_c values are independent of the carrier gas flow-rate supports a basic boundary condition of the previous work[1], based on a departure from equilibrium at the liquid–gas interphase boundary. Eqn. 4 is derived with the help of this condition. In contrast with that, the assumption of equilibrium at the liquid–gas interphase boundary has been shown[1] to lead to profound disagreement with the experimental results, since in that case the k_c values must be different for various carrier gas flow-rates.

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