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DETERMINATION OF RATE COEFFICIENTS AND DIFFUSION COEFFICIENTS OF BUTANOL USING RF-GC METHODOLOGIES

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ABSTRACT. Reversed-flow gas chromatography, which is a sub-technique of inverse gas chromatography, is an experimental arrangement simulating a simple model for the action of liquid pollutants in laboratory scale. By using a commercial gas chromatograph and an appropriate mathematical analysis, kinetic parameters such as rate coefficients, k_c and diffusion coefficients, D of analyzed liquid were calculated. These physicochemical properties of the liquid experimented will contribute to the references for future research in the area of environment, food, agriculture as well as physical sciences.

Keywords: *Chromatography, Diffusion Coefficient, Evaporation, Pollutant, Rate Coefficient*

INTRODUCTION

Evaporation is a vital ecological fate for compounds introduced into both freshwater and marine environments by accidental spills, industrial effluents, or introduced directly into the air from industrial unit processes such as bioreactors and cooling towers. Atmosphere contains many gases that homogeneously distributed such as, carbon monoxide, nitrogen oxides, sulphur oxides, petroleum hydrocarbons and pesticides. These pollutants attack solids; including historical buildings and monuments that are finally malformed to permanently damaged products. Gases also pollute seawater, transferred from the atmosphere to the water surface and then dissolved into the liquid phase. The transfer rate of pollutants from the air onto the sea surface depends on rate coefficients and diffusion coefficients in the gas phase [1].

The first idea on reversed-flow gas chromatography (RF-GC) differential aspect was that of Phillips and co-researchers[2], who stopped the flow of the carrier gas for a short time period repeatedly, producing each time extra narrow peaks. By this method, he measured the differential rate of a catalytic

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reaction-taking place on the stationary phase in a gas chromatographic column. The method permitted a direct determination of reaction rates, not only for small conversions to products, or for reaction times around zero, but in the whole range of conversions covering an extended period of time [3].

The aim of the research was to determine the rate coefficients and diffusion coefficients of butanol under study assisted by RF-GC techniques.

RESULTS AND DISCUSSION

The results obtained from the preliminary experiments were evaluated for physicochemical quantities of butanol.

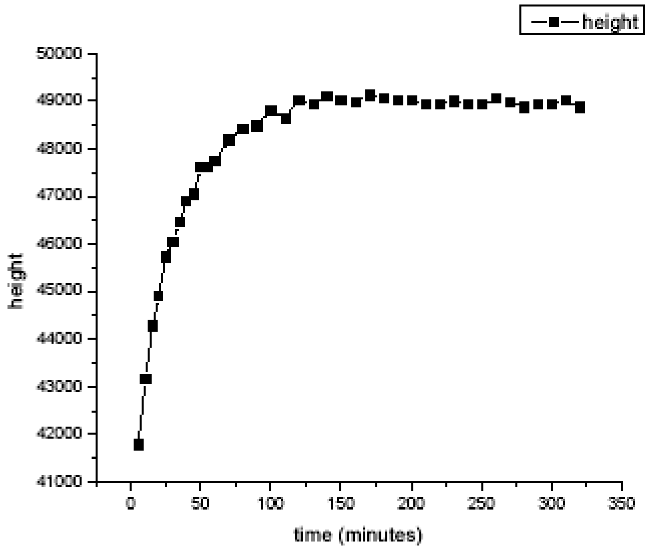

Figure 1. The rise of the sample peak height with time for the diffusion of butanol vapor into nitrogen (V=cm^3 s-^{1}), 313.15K and 1 atm.

In Figure 1, the height, h of the sample peaks as a function of the time t_0, when the flow reversal was made, is plotted on a semilogarithmatic scale [4]. It shows the steep rise and then the leveling off with time of the sample peak height. As an example using equation,

$$\ln(h_\infty - h) = \ln h_\infty - [2(k_c L + D)/L^2]t_0 \qquad \textbf{Equation 1}$$

$$\ln[h(L/2t_0^{1/2} + k_c t_0^{1/2})] = \ln[4k_c c_0/v(D/\pi)^{1/2}] - (L^2/4D)(1/t_0) \qquad \textbf{Equation 2}$$

which derived from Katsanos [5] to analyze the experimental findings, the data on Figure 1 are treated as follows. Iterated some points, which correspond to small times, the rest of the experimental points are plotted according to Equation 1, as shown in Figure 2.

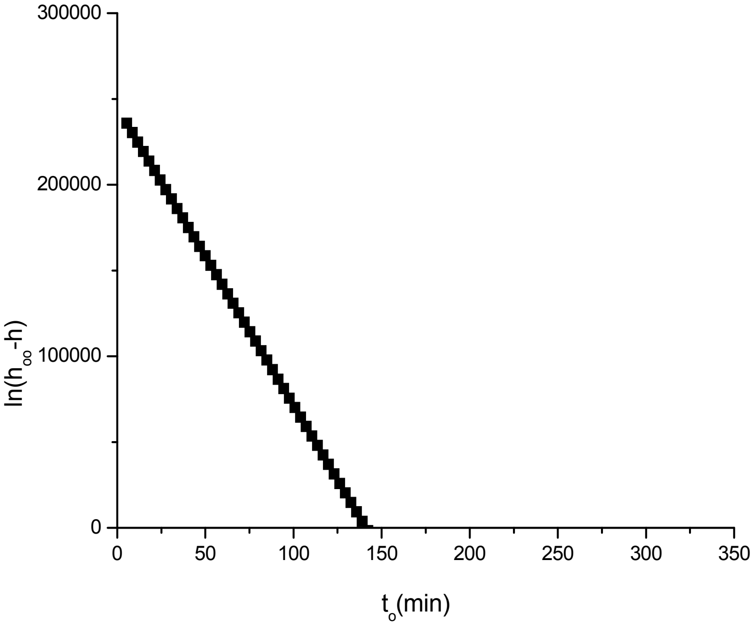

Figure 2. Diffusion of butanol vapor into nitrogen (V=1cm^3 s^{-1}), at 313.15K and 1atm.

As infinity value h_∞ was taken the mean of the values found in the time interval, which differed little from one another. From the slope of this plot, which is equal to - $2(k_cL+D)/L^2$, according to Equation 1, using the theoretically calculated value of 0.1020 cm^2 s^{-1}, and the actual value of L (28.5cm), a value of 208.68 cm s^{-1} for k_c, is calculated.

This approximate value is now used to plot all but the few point closed to h_∞ according to Equation 2 as shown in Figure 3.

From the slope of this latter plot, a value of 0.1020 cm^2 s^{-1} for *D* is found. If this is combined with the slope of the previous plot (Figure 2), a second value for k_c= 208.68 cm s^{-1} is calculated and further used to replot the data according to Equation 2. The new value for *D* found coincides with the previous one (0.1020 cm^2 s^{-1}), and thus the iteration procedure must be stopped.

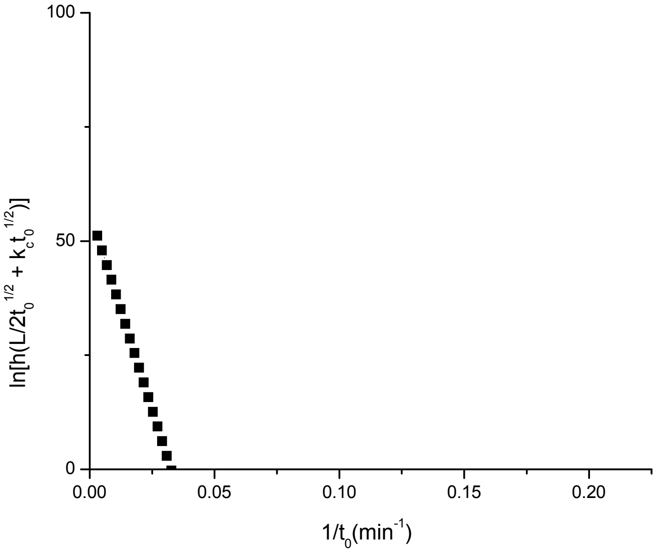

Figure 3. Data from evaporation of butanol into nitrogen ($V=1\mathrm{cm}^3\,\mathrm{s}^{-1}$), at 313.15K and 1atm.

Table 1. Rate Coefficients for Evaporation of Pure Liquid and Diffusion Coefficients of Vapors Into Nitrogen at 1atm

			D, $\mathrm{cm}^2\,\mathrm{s}^{-1}$		
Liquid	T, K	k_c, $\mathrm{cm\,s}^{-1}$	This work	Theoretical	Deviation (%)
Butanol	313.15	208.68±0.08	0.1020±0.0005	0.1020	0.01
	323.15	218.75±0.04	0.1079±0.0015	0.1078	0.13
	333.15	229.80±0.12	0.1137±0.0004	0.1137	0.04
	343.15	241.65±0.05	0.1197±0.0002	0.1197	0
	353.15	254.39±0.10	0.1259±0.0001	0.1259	0
	363.15	268.08±0.07	0.1322±0.0008	0.1322	0.04
	373.15	283.57±0.02	0.1386±0.0002	0.1387	0.07

Table 1 summarizes the results obtained with the pure liquid studied. In the same table, the diffusion coefficients determined here are compared with those calculated theoretically. As one can see from the Table 1, the *D* values determined in this work are very close to the theoretical ones. The deviation given in the last column is the accuracy of the experimental values from those calculated theoretically [6]:

$$\text{Deviation (\%)} = 100[(D_{\text{found}}-D_{\text{theory}})/D_{\text{found}}]$$

With no exception, this accuracy is better than 0.5% in all cases and indicated that investigation of liquid pollutants using reversed-flow gas chromatography (RF-GC) is of great significance in environmental science. However, the comparison of experimental and literature values is impossible because the experimental temperatures, column length, gas flow rate and pressure are varies [7].

Evaporation of chemicals from water bodies to the atmosphere can be an important environmental pathway for certain pollutant liquids. The transfer rate of pollutants from the air onto the sea surface depends on rate coefficients and diffusion coefficients in the gas phase. The chemical interaction involves measurement of the rate of liquid loss into a gas stream flowing horizontally across the liquid surface. In the majority of these techniques relative evaporation rates, which cannot be related to the physical properties of the evaporating species, as well as evaporation halftimes are measured. Thus, this relative new technique of reversed-flow gas chromatography (RF-GC) is suitable to study various physicochemical measurements, such as of rate coefficients and diffusion coefficients for the evaporation of pure liquid.

CONCLUSIONS

The uniqueness of the method is its accuracy and simplicity. The presented style of reversed-flow gas chromatography can be used to simultaneously determine correct absolute evaporation rates and vapours diffusivities of pure liquids.

EXPERIMENTAL SECTION

In this type of chromatography, the column is unfilled with any material and sampling process is carried out by reversing of the carrier gas from time to time producing sample peaks. Selected liquid pollutants of 99.99% purity (MERCK) will be used as solute, while carrier gas was nitrogen of 99.99% purity. After the injection of 1 cm^3 s^{-1} of liquid pollutant at atmospheric pressure and selected temperature, a continuous concentration–time curve is record passing through a maximum and then declining with time. By means of a six-port valve, the carrier gas flow direction is reversed for 5 s, which is a shorter time period than the gas hold-up time in both column sections l and l', and then the gas is again turned to its original direction. This procedure creates extra chromatographic peaks (sample peaks) superimposed on the continuous elution curve. This is repeated many times during the experiment lasting a few hours. The height, h of the sample peaks from the continuous signal, taken as baseline, to their maximum is plotted as ln (h_∞-h) versus time, giving a *diffusion band*, whose shape and slope both depend on vessel L which is empty, as well as on the geometric characteristics of the vessel and the temperature. In all experiments, the pressure drop along l + l' will negligible, while the carrier gas flow-rate will keep constant (1.0 cm^3 s^{-1}).

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