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# A Site-Specific and Multielement Approach to the Determination of Liquid-Vapor Isotope Fractionation Parameters. The Case of Alcohols

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Isotope fractionation phenomena occurring at the natural abundance level in the course of liquid-vapor transformation have been investigated by using the SNIF-NMR method (site-specific natural isotope fractionation studied by NMR) which has a unique capability of providing simultaneous access to fractionation parameters associated with different molecular isotopomers. This new approach has been combined with the determination of overall carbon and hydrogen fractionation effects by isotope ratio mass spectrometry (IRMS). The results of distillation and evaporation experiments of alcohols performed in technical conditions of practical interest have been analyzed according to the Rayleigh-type model. In order to check the performance of the column, unit fractionation factors were measured beforehand for water and for the hydroxylic sites of methanol and ethanol for which liquid-vapor equilibrium constants were already known. Inverse isotope effects are determined in distillation experiments for the overall carbon isotope ratio and for the site-specific hydrogen isotope ratios associated with the methyl and methylene sites of methanol and ethanol. In contrast, normal isotope effects are produced by distillation for the hydroxylic sites and by evaporation for all the isotopic ratios. The effective fractionation factors obtained from least-squares treatment of the data have been analyzed in terms of liquid-vapor equilibrium fractionation factors and in terms of kinetic evaporative fractionation factors associated either with the whole set of isotopomers or with the individual isotopic species. Suitable conditions for an accurate determination of the relative values of these parameters are provided by the proposed approach which gives access to several fractionation factors in a one-pot experiment. From a practical point of view, the unit fractionation factors determined in this work provide a quantitative basis for correcting the isotope ratio of the ethanol isotopic probe for physical effects due to distillation and evaporation.

## Introduction

Phase transition, transport phenomena, and technological treatment are generally accompanied by isotope fractionation. The equilibrium distribution of isotopes in water, in particular, varies significantly between the different physical states and depends on the climatic environment.<sup>1-6</sup> In the case of hydrogen, a liquid (L)-vapor (V) fractionation factor,  $\alpha_e$ , can be defined as

$$\alpha_e = \frac{(D/H)_V}{(D/H)_L} = \frac{R_V}{R_L} \quad (1)$$

where  $D/H = R$  represents the ratio of the numbers of deuterium and protium isotopes. Vapor water is depleted in deuterium as shown by the value of  $\alpha_e$  less than unity determined at several temperatures.<sup>1,2</sup> This property, which is related to the vapor pressure difference between  $H_2O$  and  $HDO$ , explains the deuterium enrichment of the remaining water in a distillation process operating under equilibrium conditions. Evaporation also produces an increase in the deuterium content of the remaining water. This enrichment is governed by both the evaporation kinetic isotope effect and an isotopic exchange between the atmospheric moisture and the liquid.<sup>3-10</sup> The investigation of these phenomena requires accurate determination of isotope ratios. Such measurements are conveniently performed by isotope mass spectrometry, but this method gives access only to an overall isotope ratio of the molecule. Therefore, it does not directly apply to the study of individual isotopomers in multisite molecules. Moreover, interest has been mainly focused on the case of water and less is known on the

influence of phase transitions and physical processes on the isotope fractionation of carbon, hydrogen, and oxygen in alcohols.

We have shown that deuterium is usually far from being randomly distributed among the different sites of a given molecular species.<sup>11</sup> On this basis site-specific natural isotope fractionation studied by NMR (SNIF-NMR) is of great potential for a better understanding of hydrogen filiations in chemical or biochemical syntheses.<sup>12,13</sup> In this paper we show that the method also offers a unique capability of simultaneously measuring isotope fractionation of hydrogen in several individual molecular sites under the influence of a physical transformation such as distillation and evaporation. This approach, which exploits the natural abundance distribution of deuterium, avoids the need for a separate investigation of selectively enriched materials. Moreover, since several sites can be compared in a single experiment it provides optimum conditions for an accurate determination of the relative values of equilibrium liquid-vapor fractionation factors of isotopomers. We shall focus our interest on the case of ethanol which constitutes a powerful probe for inferring the isotopic behavior of precursor carbohydrates in photosynthesis.<sup>14</sup> The analysis of isotope effects in terms of mechanistic and environmental effects then requires that fractionation phenomena possibly occurring in the course of extraction, isolation, and storage of ethanol be fully appraised. It is therefore interesting to investigate the effects of equilibrium and kinetic fractionation factors on the overall carbon-13 content and on the populations of the monodeuterated methyl (I) and methylene (II) isotopomers.

## Experimental Section

(a) *Distillation.* Several series of experiments were performed with a Cadiot spinning band distillation column and with a packed column using alcohol samples characterized by isotopic ratios  $R_Q$ .

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TABLE I: Isotopic Data of the Water and Alcohol Samples Used in This Study<sup>a</sup>

	<i>t</i> , wt %	(D/H) <sub>CH<sub>3</sub></sub>	(D/H) <sub>CH<sub>2</sub></sub>	(D/H) <sub>OH</sub>	( $\overline{D/H}$ )	$\delta(^{13}\text{C})$
H <sub>2</sub> O			150			
CH <sub>3</sub> OH	99.9	129.1		139.8	131.8	-45.7
CH <sub>3</sub> CH <sub>2</sub> OH	99.87	93.0 <sub>3</sub>	129.5	138.5	112.8	-28.5
	99.68 <sup>b</sup>	108.8 <sub>3</sub>	133.5	149.6	126.6	-31.1
	9.52	93.4	125.1	150.0	115.4	-27.2
	9.65	94.0	123.9	150.0	113.3	-26.7
	81.94					-27.2
	89.50					-27.2
	91.09	93.8	125.3	158.0	115.0	-27.2
	99.93					-27.2

<sup>a</sup>The D/H ratios are expressed in ppm and the  $\delta(^{13}\text{C})$  parameter, defined in eq 7, is expressed in ‰ with respect to PDB. *t* is the alcoholic grade in weight. The methanol sample is from a synthetic origin. Ethanol is from the fermentation of beet sugar except in case *b* which corresponds to a synthetic sample. The  $\delta(^{18}\text{O})$  value of the water sample which is equal to -5.6‰ obeys the meteoric relationship with the deuterium parameter.<sup>4-16</sup>

In a given set of experiments, either pure alcohol or an alcohol-water mixture was subjected to *n* separate distillations performed under strictly identical conditions but stopped at different fractions of transformation,  $\rho$ . The distillations were carried out under high reflux (40 to 1 reflux ratio) and slow product rate. For every volume of distillate, *D*, the mass, *m<sub>D</sub>*, and the alcoholic grade, *t<sub>D</sub>* (w/w), of the ethanol were measured and the sample was directly subjected to the mass spectrometry or SNIF-NMR analysis for the determination of *R<sub>D</sub>*. The mass, *m<sub>L</sub>*, the alcoholic grade, *t<sub>L</sub>*, and the isotopic ratio, *R<sub>L</sub>*, of the remaining alcohol were also measured. From a general point of view, the isotopic enrichment produced in fractionating columns has been shown to be related to the number of theoretical plates, *P*, to the reflux coefficient, *p*, and to the equilibrium liquid-vapor fractionation factor,  $\alpha_e$ , by a transcendental equation.<sup>20-22</sup> However, we can estimate the errors on the  $\alpha_e$  values resulting from the approximation of total reflux adopted in the analysis of our data (eqs 8 and 9). Thus when the reflux rate remains less than 0.03 in a column with a theoretical number of plates *P* = 8 the error on a fractionation factor  $\alpha_e$  of about 1.003 does not exceed 0.0003.

In the case of water-alcohol mixtures, the distillation of the remaining liquor was conducted to completion under the same reflux in order to obtain a sample of pure alcohol suitable for the measurement of *R<sub>L</sub>*. In practice, the yield of the ethanol extraction then reached 98.5–99%. In these conditions, residual isotope fractionation may be associated with the extraction process. This effect can be estimated by means of eq 5, using values of the unit fractionation factor  $\alpha$  previously determined in the experiments performed with pure ethanols. It is negligible with respect to the precision of the D/H determinations in the case of hydrogen, and it was corrected for in the case of carbon. Both *R<sub>D</sub>*/*R<sub>Q</sub>* and *R<sub>L</sub>*/*R<sub>Q</sub>* ratios are therefore accessible in all experiments and the unit fractionation factors,  $\alpha$ , can be evaluated by means of eqs 3 and 5, respectively.

It can be noted that the isotope content of the hydroxylic site of the starting material is strongly dependent on the preparation of the sample. When highly concentrated ethanol obtained from rectification is used, the remaining water is strongly enriched and this enrichment is transmitted to the ethanol site, III, by chemical exchange. Due to these exchange phenomena, the isotopic contents associated with the hydroxylic site of ethanol-water mixtures generally exhibit more complex behavior and their variations will not be analyzed in detail.

A sample of water was also distilled under the same experimental conditions in order to check the performances of the column and to compare the values of the unit fractionation factors of hydrogen, <sup>2</sup> $\alpha$ , and of oxygen, <sup>18</sup> $\alpha$ , to those of the equilibrium fractionation factors given in the literature.

(b) *Evaporation*. A series of *n* identical flasks, filled with the same alcoholic mixture (mass *m<sub>Q</sub>*, alcoholic grade *t<sub>Q</sub>*), were allowed to evaporate at constant temperature, and at atmospheric pressure during a period of time  $\tau$  (h). The mass, *m<sub>L</sub>*, and the alcoholic grade, *t<sub>L</sub>*, of the remaining liquid were measured for each experiment corresponding to a given value of  $\tau$  and the amount of evaporation,  $\rho$ , was calculated. The remaining liquids, *L*, were then distilled as described in subsection a in order to determine

the values of the isotope ratios *R<sub>L</sub>*. The evaporation was performed at several temperatures and with different alcoholic solutions (*t<sub>w/w</sub>* = 0.8–0.9). The effective kinetic isotope effects,  $\beta_{\text{eff}}$ , defined according to the model of eq 15 were computed from appropriate treatment of the Rayleigh-type equations (subsection d).

(c) *Analytical Determinations*. Anhydrous ethanol was obtained from pure beet-root alcohol which was carefully dried on 3 Å molecular sieves. The water-alcohol mixtures used in the distillation experiments were prepared from precisely weighed amounts of pure beet-root ethanol and water and the alcoholic grades were checked by volumetric titration (chromic oxidation). The alcoholic grades of all the distillates and those of the starting solutions used in the evaporation experiments were determined by the Karl-Fisher procedure. The isotope ratios were measured by mass spectrometry (Finnigan Delta E for <sup>13</sup>C and <sup>18</sup>O and VG instruments Sira 9 for deuterium) and by <sup>2</sup>H NMR (Bruker AM400). They are reported on the PDB<sup>15</sup> (<sup>13</sup>C) and V. SMOW<sup>16</sup> (<sup>2</sup>H, <sup>18</sup>O) scales. The experimental conditions and the referencing procedures for the SNIF-NMR experiments are described in ref 17. Ten series of NMR spectra (128 scans) were run for every sample. The precision and the accuracy of the NMR determinations are optimized by automation of the measurement (automatic sample changer) and of the data collection. The statistical treatment was carried out with specific software running on IBM-AT and MicroVAX Digital computers which are networked with the dedicated computer of the spectrometer.

The precision on the yield of the transformation,  $\rho$ , is better than 0.2% and the precisions on the isotope ratios, *R<sub>D</sub>* and *R<sub>L</sub>*, are of the order of 0.01% for carbon and 0.2% for the methyl and methylene hydrogen parameters of methanol and ethanol. A Lorentzian least-squares procedure was used for estimating the area of the hydroxylic deuterium signal which is relatively broad. The precision is not better than 1% in this case. The isotope ratios of the starting samples used in this study are collected in Table I.

(d) *Treatment of the Data*. Due to the flattened shape of the theoretical dependency of the fractionation ratio on the yield of the transformation (eqs 3–5), a linear least-squares treatment involving a logarithmic transformation is not convenient for handling the data. We have developed an iterative nonlinear procedure, founded on the algorithm of Gauss-Marquardt,<sup>18</sup> which is run on an IBM-AT computer (DOS 3.3). In the present case the least-squares minimization with respect to only one parameter,  $\alpha$  (or  $\beta_{\text{eff}}$ ), reduces to the computation of a Jacobi vector  $\mathbf{J} = \partial f(x_i)/\partial \alpha$  which leads to the scalar  $B = \mathbf{J} \cdot \mathbf{J}$

$$B = \sum_{i=1}^m ((\ln x_i) x_i \alpha)^2$$

where  $f(x_i)$  is the difference between the estimation,  $\hat{y}_i$ , and the actual value,  $y_i$ , of the dependent variable.

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Denoting  $g$  the cross product  $\bar{J}f(x_i)$ , the iterated value of the coefficient  $\alpha$  is equal to  $-g/B$ . Usually fewer than six iterations are needed to achieve a computational precision in agreement with the experimental precision (0.0001 for  $^{13}\alpha$  and 0.001 for  $^2\alpha$ ). The least-squares procedure may be also applied to the case of two parameters ( $\alpha$  and  $R_Q$ ) in order to check the consistency of the whole experimental set of data.

## Results and Discussion

(a) *Distillation.* In a distillation process, where the unit fractionation factor,  $\alpha$ , defined in eq 2 may be considered as being constant in the course of the transformation, the isotope ratio,  $R_L$ , of the remaining material, L, follows a simple kinetic equation of the Rayleigh type <sup>34,19</sup>

$$\alpha = \frac{dN_h}{dN_l} \bigg/ \frac{N_h}{N_l} \quad (2)$$

$$R_L = R_Q(1 - \rho)^{\alpha-1} \quad (3)$$

In these equations,  $N_h$  and  $N_l$  are the numbers of molecules bearing the light, l, and the heavy, h, isotopes and the isotope ratio  $R$  is defined as the ratio of the numbers of heavy and light isotopes

$$R = N_h/PN_l \quad (4)$$

where  $P$  is the number of equivalent molecular positions which can be occupied by the h tracer.  $\rho$  is the yield of the transformation and  $R_Q$  is the isotope ratio of the starting material.

The isotope ratio of the distillate,  $R_D$ , then obeys an equation of the type

$$R_D = R_Q(1/\rho)[1 - (1 - \rho)^\alpha] \quad (5)$$

The unit fractionation factor,  $\alpha$ , can be computed from nonlinear regression analyses carried out on eqs 3 or 5. It can also be obtained from the ratio of the intercepts of curves 5 and 3 at  $\rho = 0$

$$\alpha = \left( \frac{R_D}{R_Q} \right)_{\rho \rightarrow 0} \quad (6)$$

These kinetic equations can also be expressed in terms of the relative isotope content,  $\delta\text{‰}$ , defined as

$$\delta_X\text{‰} = \frac{(N_h/N_l)_X - (N_h/N_l)_{\text{ref}}}{(N_h/N_l)_{\text{ref}}} 1000 \quad (7)$$

In this  $\delta$  scale, the deuterium and carbon-13 contents of sample X are referred to those of the V.S.M.O.W.<sup>16</sup> and PDB<sup>15</sup> references, respectively.

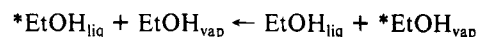
The liquid-vapor fractionation factors  $\alpha_e$ , defined as in eq 1 for the hydrogen of water, can be directly measured in distillation experiments conducted in such a way that the isotopic species removed at every instant are in thermodynamic equilibrium with the remaining medium. However, this situation which is referred to as pure Rayleigh distillation is detrimental to the precision since the variations exhibited by the isotope ratios remain very small. Higher variations are obtained with the distillation columns used in this work; however, the unit fractionation factors  $\alpha$  then depend not only on  $\alpha_e$  but also on the properties of the column. When a column k, characterized, for the isotopic species, i, by a number of theoretical plates  $P_k^i$ , is used under the experimental conditions described above, the unit fractionation factor  $\alpha_k^i$  is approximately related to the equilibrium liquid-vapor fractionation factor,  $\alpha_e^i$ , by eq 8.<sup>20-22</sup>

$$\ln(1/\alpha_k^i) \approx [(1/\alpha_e^i) - 1]P_k^i \quad (8)$$

Since the number of theoretical plates of the column may be assumed to be nearly independent of the isotopic species, i, the method provides very favorable conditions for comparing the liquid-vapor fractionation factors of the different isotopomers of a given molecule. Thus for all couples of isotopomers i and j, equations of type 9 which involve unit fractionation factors obtained in the same distillation experiment are satisfied

$$\frac{(1/\alpha_e^i) - 1}{(1/\alpha_e^j) - 1} \approx \frac{\ln(1/\alpha_k^i)}{\ln(1/\alpha_k^j)} = r_{ij} \quad (9)$$

If we consider the liquid-vapor equilibrium of ethanol, the naturally labeled molecules, denoted by an asterisk, are either the species bearing a C-13 in each of the two ethyl positions, or the methyl (I), methylene (II), or hydroxyl (III) monodeuterated isotopomers



The  $^{13}\text{C}/^{12}\text{C}$  and overall D/H ratios determined by mass spectrometry characterize the mean isotope content of ethanol whereas the NMR determinations provide values of the site-specific (D/H)<sub>I</sub>, (D/H)<sub>II</sub>, and (D/H)<sub>III</sub> ratios. In a liquid-vapor equilibrium involving the monodeuterated methylene isotopomers, for example, the equilibrium constant  $K^{\text{II}}$  is

$$K^{\text{II}} = \frac{[\text{CH}_3\text{CHDOH}]_{\text{vap}}[\text{CH}_3\text{CH}_2\text{OH}]_{\text{liq}}}{[\text{CH}_3\text{CH}_2\text{OH}]_{\text{vap}}[\text{CH}_3\text{CHDOH}]_{\text{liq}}} \quad (10)$$

In a pure Rayleigh distillation, operating under equilibrium conditions, the unit fractionation factor would be equal to this equilibrium constant. A site-specific liquid-vapor equilibrium fractionation factor is thus defined as

$$^2\alpha_e^{\text{II}} = K^{\text{II}} = \frac{(\text{D}/\text{H})_{\text{II vap}}}{(\text{D}/\text{H})_{\text{II liq}}} \quad (11)$$

Specific fractionation factors for the other molecular sites are defined in a similar way.

In order to check the performances of the distillation procedure we have first considered the case of water for which liquid-vapor equilibria have been extensively studied.<sup>2,10,20,23-25</sup> Two samples of water, one sample of methanol, two samples of pure ethanol, and two different water-alcohol mixtures containing about 10% w/w of ethanol have been subjected to series of separate distillations conducted under identical technical conditions. The isotopic parameters of the starting materials,  $R_Q$  (Table I), the yields,  $\rho$ , and the carbon and hydrogen isotope ratios of the remaining liquids ( $R_L$ ) and of the distillates ( $R_D$ ) were carefully measured. In the case of water, the oxygen isotope parameter,  $\delta(^{18}\text{O})$ , was also determined. Several experiments were carried out at small values of the yield in order to optimize the extrapolation of the distillation curve at zero yield (eq 6). The performances of two different systems, a spinning-band column and a packed column, were compared. Typical experimental data corresponding to the case of pure ethanol are represented in Figures 1-3. It is worth emphasizing that two types of behavior can be observed. In the case of water and the hydroxylic sites of alcohols (Figure 1), both the initially depleted distillate and the remaining liquid are progressively enriched whereas for carbon (Figure 2) and for the methyl and methylene hydrogens (Figure 3), the first fractions of the distillate are significantly enriched in the heavy isotope and the remaining liquid is progressively depleted. It is shown that Rayleigh-type kinetics are obeyed by the isotope ratios of the remaining liquid  $R_L$  (eq 3) and of the distillate  $R_D$  (eq 5). Nonlinear least-squares treatment of the data provides values of the unit fractionation factors given in Table II. The consistency of the experimental results with the theoretical model is very satisfactory and the iterative treatment, performed independently

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TABLE II: Values of the Unit Fractionation Factor Obtained from Nonlinear Least-Squares Treatment of Isotopic Data Associated with Distillation and Evaporation Experiments<sup>a</sup>

Distillation										
compound	N	T, K	t, wt %	column	$^{13}\alpha$	$^{18}\alpha$	$^2\alpha^I$	$^2\alpha^{II}$	$^2\alpha^{III}$	$^2\alpha^t$
HOH	1	373	100	SB		0.978			0.903	
	2			SB		0.983			0.923	
	3			PC		0.977			0.912	
CH <sub>3</sub> OH	4	338	99.87	SB	1.0020		1.015		0.812	0.951
	5			PC	1.0014		1.0095		0.861	0.964
CH <sub>3</sub> CH <sub>2</sub> OH	6	351.4	99.87	SB	1.0034		1.025	1.020	0.820	
	7		99.68	SB	1.0037		1.025	1.019	0.813	0.986
	8			PC	1.0033		1.026	1.021	0.805	0.985
	9		9.52	SB	1.0033		1.011	1.011		
	10		9.65	SB	1.0039		1.013	1.013		
Evaporation										
compound	N	T, K	t, wt%		$^{13}\beta_{\text{eff}}$	$^2\beta_{\text{eff}}^I$	$^2\beta_{\text{eff}}^{II}$	$^2\beta_{\text{eff}}^t$		
CH <sub>3</sub> CH <sub>2</sub> OH	11	295	81.94		0.995 <sub>0</sub>					0.952
	12	278	89.50		0.997 <sub>5</sub>					
	13	295	91.09		0.996 <sub>0</sub>	0.970	0.965			
	14	295	99.93		0.996 <sub>5</sub>					

<sup>a</sup>The  $\alpha$  parameter associated with distillation experiments is defined in eq 2 and calculated by means of eq 3, 5, and 6. The  $\beta_{\text{eff}}$  parameter associated with evaporation experiments is calculated by using eq 12 and 15.  $t$  is the alcoholic grade in weight of the starting material and  $T$  is the temperature of the experiment. The distillations were performed with a spinning band (SB) or a packed (PC) column. The values of  $^{2}\alpha^I$  given in the last column result from measurements of the overall deuterium content of the alcohol by mass spectrometry. The confidence interval is 0.0004 (95%) for the unit fractionation factor of carbon in the distillation experiments performed on pure alcohols. It is about 0.003 for deuterium in the methyl and methylene sites. The accuracy of the determinations is slightly lower in other measurements performed on water-alcohol mixtures (0.0006 for  $^{13}\text{C}$ , 0.006 for  $^2\text{H}$ ).

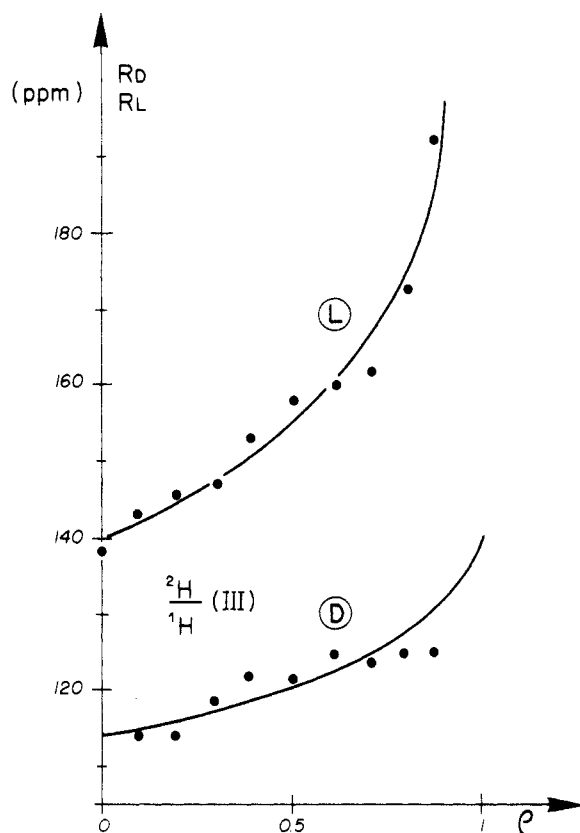


Figure 1. Variations in the deuterium isotope content of the hydroxyl site of pure ethanol (III) as a function of the yield of distillation ( $N = 6$  in Tables II and III). The accuracy of the surface measurements of the  $^2\text{H}$  NMR signals is lower for the hydroxyl than for the methyl and methylene isotopomers. A value  $^{2}\alpha = 0.820$  derived from nonlinear least-squares treatment of the experimental data has been used for calculating the simulated curves. If a value  $^{2}\alpha_e = 0.975$  is adopted for the equilibrium liquid-vapor fractionation factor associated with the  $\text{CH}_3\text{CH}_2\text{OD}$  species, the theoretical number of plates of the spinning-band distillation column calculated from eq 8 is  $P \approx 8$ .

on the isotopic data for the distillate and for the remaining liquid, are in good agreement (Figures 1–3).

These results are consistent with the normal isotope effects observed for  $\text{HDO}$  and  $\text{CH}_3\text{OD}$ <sup>2,26</sup> and with the inverse isotope

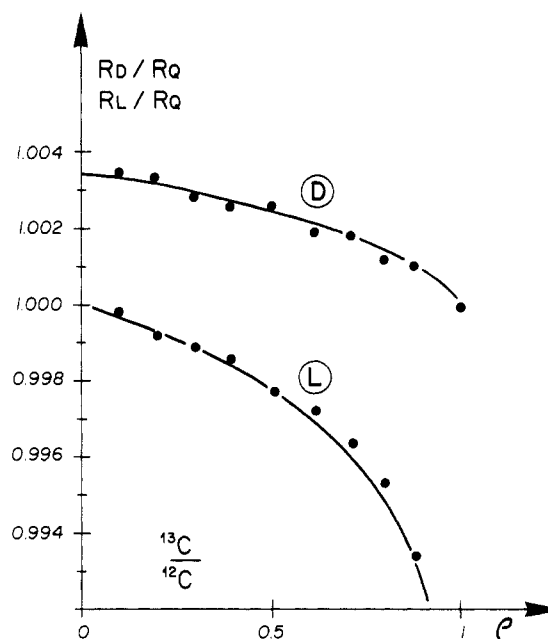


Figure 2. Variation in the overall carbon-13 content of pure ethanol as a function of the yield,  $\rho$ , of a distillation experiment. ( $N = 6$  in Tables II and III). Each point corresponds to a separate distillation experiment associated with a given value of  $\rho$ . The isotope contents have been measured by isotope ratio mass spectrometry and expressed on the  $\delta$  scale (eq 7). The values of the isotope ratios of the distillate, D, and of the remaining liquid, L, are referred to those of the starting material,  $R_Q$ :  $R_{D,L}/R_Q = (1000 + \delta_{D,L})/(1000 + \delta_Q)$ . The theoretical curves are simulated in the Rayleigh-type model (eqs 3 and 5) by using values of the unit fractionation factor  $^{13}\alpha = 1.0035$  for the distillate and  $^{13}\alpha = 1.0032$  for the residue.

effect measured for  $^{13}\text{CH}_3\text{OH}$ .<sup>26–29</sup> In the case of ethanol, inverse isotope effects are exhibited by the two  $^{13}\text{C}$  isotopomers and by

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TABLE III: Values of Equilibrium Liquid-Vapor Fractionation Factors,  $\alpha_e$ , of Alcohols ROH<sup>a</sup>

R	t, °C	N	isotopic species				ref
			HOD	H <sup>18</sup> OH			
H	100		0.974	0.995			2, 10
		1		0.994			
		2	0.974*	0.994			this work
		3		0.993			
CH <sub>3</sub>	65.5		CH <sub>3</sub> OD	CD <sub>3</sub> OH	<sup>13</sup> CH <sub>3</sub> OH		
			0.973	1.0073			27
			0.989		1.00043		26, 28, 29
			0.990	0.9951			29
			0.965	1.0120			26
			0.967				26
	64				1.00028		22
	25		0.947				30
	65	4	CH <sub>3</sub> OD	CH <sub>2</sub> DOH	<sup>13</sup> CH <sub>3</sub> OH		this work
				1.0017	1.00023		
		5	0.977*	1.0015	1.00022		
CH <sub>3</sub> CH <sub>2</sub>	75		CH <sub>3</sub> CH <sub>2</sub> OD	C <sub>2</sub> D <sub>5</sub> OH			
			0.971	1.0171			26
			0.978				32
	25		0.950				33
	78.4	6	CH <sub>3</sub> CH <sub>2</sub> OD	CH <sub>2</sub> DCH <sub>2</sub> OH	CH <sub>3</sub> CHDOH	<sup>13</sup> C	
				1.0032	1.0024	1.00043	
		7	0.975*	1.0033	1.0023	1.00046	this work
				1.0030	1.0025	1.00039	
		8					

<sup>a</sup> $\alpha_e$  refers the isotope distribution in the vapor phase to that of the liquid phase. It is defined in eq 1 for the hydrogen isotopes of water and in eq 11 for the methylenic isotopomers of ethanol. The literature values have been obtained from vapor pressure or distillation experiments. We have used reasonable mean values (\*) over literature data associated with the deuterated hydroxylic site for calculating the <sup>18</sup>O, <sup>13</sup>C and site-specific <sup>2</sup>H parameters from the unit fractionation factors determined in the distillation experiments  $N = 1-8$  described in Table II. The  $\alpha_e$  values have been calculated from eq 8 and 9. Equation 8 is strictly valid in conditions of total reflux. By taking into account the effects of a finite value of the reflux<sup>20</sup> it is estimated that the use of eq 8 and 9 may introduce an error of the order of 0.0002 on the computed values of the site-specific parameters <sup>2</sup> $\alpha_e$  (CH<sub>2</sub>) for example. This error is of the same order of magnitude as the experimental precision.

every monodeuterated methyl and methylene isotopomer. In contrast, the expected normal isotope effect is measured for the hydroxylic isotopomer. In this respect it should be emphasized that the normal isotope effect measured in a mass spectrometry determination of the overall hydrogen isotope ratio (Table II) is in fact the result of two inverse and one normal site-specific effects. The measured values are fairly consistent with the appropriate means over the site-specific parameters as expected, from eq 6, in tracer conditions. The water-alcohol mixtures behave similarly. However, in this case the results obtained for the hydroxylic hydrogen, and consequently for the overall hydrogen isotope ratio, are not readily interpretable on a quantitative basis due to isotopic exchange of the hydroxylic hydrogens between ethanol and variable proportions of water. In addition, the determination of the isotope ratio of the remaining alcohol then requires a complementary distillation as described in the Experimental Section and the accuracy of the results is lower than for pure alcohols. Nevertheless, it is shown that the computed values of the unit fractionation factors are of the same order of magnitude as those of pure ethanol (Table II). In the range of concentrations investigated, and for the carbon and carbon-bound hydrogen isotopes, ethanol can therefore be considered as evolving almost independently from water.

A number of methods have been applied to the determination of the liquid-vapor fractionation factor,  $\alpha_e$ , which is approximately equal to the ratio of the vapor pressures of the pure isotopic molecules.<sup>26</sup> Literature data obtained by independent or differential pressure measurements or by distillation techniques are collected in Table III. A number of determinations are concerned with the hydroxylic site. Therefore, we have adopted mean values of  $\alpha_e^{\text{OD}}$  for calculating the other overall or site-specific separation factors,  $\alpha_e^i$ , from the experimental values of the unit fractionation factors,  $\alpha_k^i$  (Table II), using eq 9. These determinations are given in Table III. The results concerning the <sup>18</sup>O parameter of water

and the deuterium and <sup>13</sup>C parameters of methanol are in agreement with the literature data which are themselves somewhat scarce. Very close values of the inverse isotope effect are calculated for the methyl and methylene isotopomers of ethanol and it is likely that both carbon-13 isotopomers also exhibit similar inverse separation factors. This behavior is consistent with known properties of isotopic substitution. Thus the smaller vapor pressure exhibited by the CH<sub>3</sub>CH<sub>2</sub>OD species with respect to the light molecule is in agreement with the general behavior of species strongly associated in the condensed phase whereas the higher vapor pressure associated with the CH<sub>2</sub>DCH<sub>2</sub>OH, CH<sub>3</sub>CHDOH, and C-13 isotopomers is frequently observed for nonassociated isotopic sites.<sup>26</sup> Vapor pressure isotope effects can be explained in terms of the influence of the intermolecular forces on the motions of molecules in the condensed material.<sup>31</sup> In the case of the hydroxylic hydrogen, the change in the external motions produced by the intermolecular potential present in the condensed state is the predominant contribution and gives rise to a normal isotope effect.<sup>32,33</sup> However, the intermolecular forces in the condensed phase are also the source of disturbances of the energy levels characterizing the intramolecular motions, and either inverse or normal isotope effects may result from this contribution. Thus the vapor pressure of deuterated methanol, CD<sub>3</sub>OH, is higher than that of the fully protonated species and inverse isotope effects of about 1.007 and 1.012 at 293 K have been reported.<sup>26,27</sup> Similarly higher vapor pressures of the carbon-13 substituted molecule with respect to the light molecule have been detected.<sup>28,22</sup> Our results are in good quantitative agreement with the existing observations and the new results obtained for ethanol are quite consistent with the expected behavior.

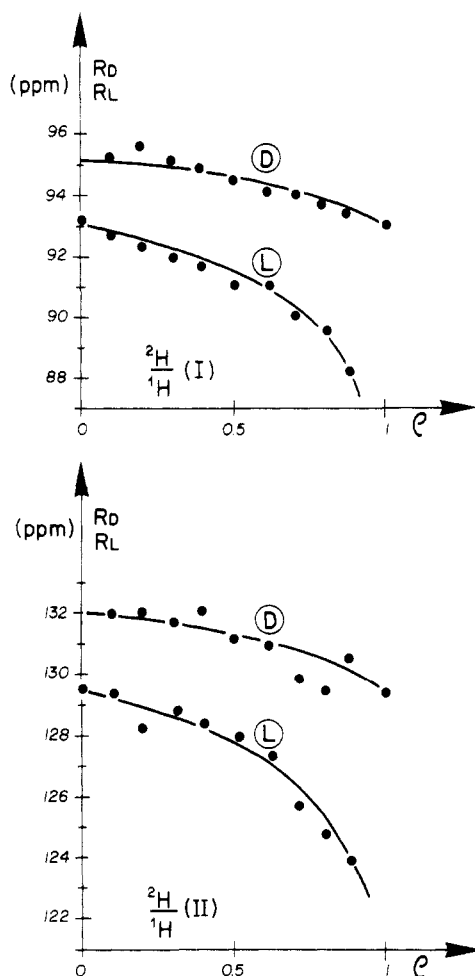
(b) *Evaporation.* If a molecular species in the liquid state, A<sub>l</sub>, simply evaporates into an atmosphere assumed to be completely

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**Figure 3.** Variations in the specific deuterium isotope contents of the methyl (I) and methylene (II) sites of pure ethanol as a function of the yield,  $\rho$ , of distillation ( $N = 6$  in Tables II and III). The results have been obtained by the NMR method. They are expressed in ppm on the D/H scale. The theoretical curves are simulated in the Rayleigh-type model (eqs 3 and 5). The same value has been retained for simulating the isotopic behavior in the distillate and in the residue. This value  ${}^2\alpha_l = 1.023$  or  ${}^2\alpha_{II} = 1.020$  (II) is the mean over the values derived from the nonlinear least-squares treatment of the experimental data for the distillate and the residue (which do not differ by more than 0.003).

free of vapor molecules,  $A_v$ , the isotope ratio of the remaining material,  $R_L$ , is diffusion-controlled and follows a Rayleigh-type kinetic equation

$$R_L = R_Q(1 - \rho)^{\beta^{\dagger}-1} \quad (12)$$

in which  $\beta^{\dagger}$  is the kinetic isotope effect of the evaporation process. For the water-alcohol mixtures investigated in this work this assumes that ethanol and water evaporate independently of each other.

In the case of water, pure evaporative processes are seldom encountered due to the presence of atmospheric moisture. Liquid-vapor isotopic exchange must also be taken into account and several models have been proposed to interpret the fractionation phenomena intervening in practical experimental conditions.<sup>3-10,34</sup> In particular, evaporation accompanied by an exchange with atmospheric vapor characterized by a constant isotope ratio,  $R_v$ , may be a realistic situation for certain water evaporation processes.<sup>10</sup> In the case of ethanol, it is more appropriate to consider a possibility of exchange with the ethanol vapor formed at the liquid surface by the net evaporation process. In this situation the isotope ratio of the local vapor,  $R_v$ , remains proportional to that of the liquid,  $R_L$ .

If  $h$  is the relative humidity in ethanol of the exchanging atmosphere,  $R_v$  can be calculated as the weighted algebraic average over the contribution  $\beta^{\dagger}R_L[1/(1-h)]$  of the evaporated fraction and  $\beta^{\downarrow}R_v/[h/(1-h)]$  of the condensed fraction and

$$R_v = \frac{\beta^{\dagger}}{1-h+\beta^{\downarrow}h} R_L \quad (13)$$

where  $\beta^{\downarrow}$  is the kinetic isotope effect for the condensation process. The kinetic parameters  $\beta^{\dagger}$  and  $\beta^{\downarrow}$  are related to the equilibrium fractionation factor  $\alpha_e$  by

$$\alpha_e = \beta^{\dagger}/\beta^{\downarrow} \quad (14)$$

The isotope ratio of the vapor removed at every instant being considered as constantly proportional to that of the liquid (eq 2)  $R_L$  evolves according to a Rayleigh-type eq 3 governed by an effective fractionation factor

$$\beta_{\text{eff}} = R_v/R_L = \frac{\beta^{\dagger}}{1-h+\beta^{\downarrow}h} \quad (15)$$

Three series of evaporation experiments have been carried out at a temperature of about 295 K with three ethanol samples of different alcoholic grades (0.8, 0.9, and 1.0 w/w). One experiment was also performed at a lower temperature 278 K (Table II). The isotope ratios were only measured on the remaining material. However, in one case the vapor fraction was trapped at a low temperature in order to check the isotopic behavior. It was then shown that a 2‰ depletion in the  ${}^{13}\text{C}$  content of the vapor with respect to the liquid ethanol ( $\delta({}^{13}\text{C}) = -26.7\text{‰}$ ) accompanies a mass loss of 1%. The mass variation,  $k$  (g/h), in the course of the evaporation obeys, as expected, a first-order kinetics which depends on the temperature and on the alcoholic grade,  $t_L$ , of the hydroalcoholic solution. At 295 K

$$k \text{ (g/h)} = 6.9 \times 10^{-4} - 4.5 \times 10^{-3}t_L \quad (16)$$

Thus for  $t_L = 0.90$  the loss of mass is of the order of 0.003<sub>5</sub> g/h. At 278 K the loss decreases to 0.002<sub>7</sub> g/h. All the overall and site-specific carbon and hydrogen isotope ratios of the remaining liquid are progressively increased in the course of the evaporation process and Rayleigh-type kinetics are satisfactorily obeyed. Within the precision of the experiment, the effective kinetic isotope effects do not vary with the alcoholic grade in the selected range. The values of the  $\beta_{\text{eff}}$  parameter at 295 K calculated by using the model discussed above are given in Table II. A slightly different value of  ${}^{13}\beta_{\text{eff}}$  for carbon is determined at 278 K:  ${}^{13}\beta_{\text{eff}} = 0.997_5$ . However, such variations remain within the limit of the experimental precision.

As in the case of the distillation, the interpretation of the kinetic parameters derived from the evolution of the hydroxylic (D/H)<sub>III</sub> ratio and of the overall average ratio, (D/H), is complicated by the isotopic exchange with water. These parameters therefore only present an empirical interest.

In the Rayleigh-type model, the effective fractionation factor depends on the evaporative fractionation factor  $\beta^{\dagger}$  and on the relative humidity in ethanol,  $h$ , according to eq 15. If it is assumed that  $h$  is negligible in the conditions of the experiment,  $\beta_{\text{eff}}$  is equal to  $\beta^{\dagger}$ . The evaporation experiments then directly measure the kinetic isotope effects for ethanol vaporization. This situation is more likely to occur in the case of ethanol than in that of water which is usually associated with high degrees of water humidity in natural conditions. The present methodology is therefore expected to provide a reliable approach to the site-specific evaporative fractionation factors.

## Conclusions

The SNIF-NMR method provides a new approach for directly determining, in a single experiment and without the need for isotopic enrichment, the unit fractionation factors of physical processes associated with the different monodeuterated isotopomers of a given molecular species. When combined with mass spectrometry determinations of overall  ${}^{18}\text{O}$ ,  ${}^{13}\text{C}$ , and  ${}^2\text{H}$  contents, the method is particularly suitable for rapidly determining accurate

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relative values of the thermodynamic liquid-vapor equilibrium constants or of the kinetic evaporative isotope effects associated with most isotopic species of the molecule.

The evolution of the site-specific and overall isotope contents of water, methanol, and ethanol in the course of distillation and evaporation experiments performed under conditions of practical interest follows Rayleigh-type kinetics, and the fractionation factors calculated from these results are in agreement with known isotopic properties of alcohols.

Values of the kinetic condensation factors,  $\beta_{\downarrow}$ , can be estimated from the values of the corresponding equilibrium,  $\alpha_e$ , and evaporative,  $\beta_{\uparrow}$ , fractionation factors by using eq 14. For example, values of  $^2\beta_{\downarrow}$  could be determined in this way for the condensation of the  $\text{CH}_2\text{DCH}_2\text{OH}$  and  $\text{CH}_3\text{CHDOH}$  isotopomers ( $^2\beta_{\downarrow} < 0.967$  at 295 K).

In addition, the unit fractionation factors determined in this work provide the basis for appraising possible variations in isotope contents due to physical transformations of the ethanol probe. When isotopic methods are used for investigating biochemical and environmental effects in the course of photosynthesis or for in-

ferring the botanical or geographical origin of precursors of alcoholic products,<sup>14,35</sup> it is of prime importance to estimate the magnitude of possible contributions due to the preparation or storage of the ethanolic sample. Using the computed fractionation factors and considering that Rayleigh-type kinetics are obeyed, the physical effects of distillation or evaporation can be estimated from a determination of the yield of the distillation or of the loss of mass during the storage or the aging process. For example, if values of  $-27\text{‰}$  and 102 ppm are measured respectively for the overall C-13 content and for the methyl  $^2\text{H}$  content of an ethanol sample distilled with a yield of 80%, using a spinning band column as described above, isotopic effects of  $-1.2\text{‰}$  ( $^{13}\text{C}$ ) and  $-0.8$  ppm ( $^2\text{H}$ ) are estimated and must be corrected for.

**Registry No.**  $^{13}\text{C}$ , 14762-74-4;  $^{18}\text{O}$ , 14797-71-8;  $\text{D}_2$ , 7782-39-0; methanol, 67-56-1; ethanol, 64-17-5.

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## Diffusional Boundary Layers in a New Steady-State Diffusion Cell

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A new diffusion cell is described which allows the permeability of membranes to be investigated. It is known that the diffusion behavior of a penetrant is influenced by the diffusional boundary layers existing on both sides of the membrane. A method is presented which enables the thicknesses of these diffusional boundary layers at the membrane to be determined by independently measurable hydrodynamic parameters.

### Introduction

Diffusion measurements are often used as a tool to investigate mass-transfer and immobilization effects within permeable materials at a molecular level.<sup>1</sup> However, the interpretation of the experimental results obtained by such measurements is sometimes very difficult. First, the intrinsic diffusion behavior of the penetrating molecules is determined for each system by a combination of mass-transfer effects and immobilization processes such as desorption or chemical reactions and by various properties of the substrate, e.g., the porosity and the surface charge density. Second, it is impossible to stir the solutions surrounding the membrane sufficiently enough to keep their concentrations absolutely uniform right up to the surfaces of the sorbing substrate. As a consequence, diffusional boundary layers at the surfaces are formed. The thicknesses of these boundary layers, and thus the mass transfer of the penetrating molecules in the solutions, are dependent on the stirring in the diffusion cell, on the viscosity of the solutions, and on the diffusion coefficient of the penetrant. The influence of the diffusional boundary layers on the results of permeation measurements has often been underestimated and thus neglected.<sup>2</sup> However, the importance of the mass transfer of the penetrants to and from the membrane surface is more and more recognized.<sup>3,4</sup>

The present paper introduces a new steady-state diffusion cell which makes the thicknesses of the diffusional boundary layers on both sides of a membrane amenable to direct and independent measurements. The membrane divides the diffusion cell into two compartments each of which contains a solution of the diffusing species in a different but constant concentration. This membrane can easily be replaced by a disklike electrode without changing

the hydrodynamic processes within the diffusion cell. Through the use of limiting current measurements the thickness of the diffusional boundary layer at the electrode can be determined experimentally in both compartments of the diffusion cell as a function of the hydrodynamic conditions applied. A mathematical description of the results is presented, which allows the thickness of the boundary layer at the electrode, and thus at the membrane,

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