Activity Coefficients of Aroma Compounds in Model Food Systems

F. Sorrentino, A. Voilley
Ecole Nationale Supérieure de Biologie
Appliquée à la Nutrition et à l'Alimentation
Laboratoire de Biologie Physico-Chimique
21100 Dijon, France

D. Richon
Ecole Nationale Supérieure
des Mines de Paris
Laboratoire de Thermodynamique
77305 Fontainebleau, France

Infinite dilution activity coefficients of aroma compounds from various chemical series were measured in model food systems (water/carbohydrates, water/polyethylene-glycols) at concentrations of various solutes. These measurements were made with a specially designed equilibrium cell. Experimental results were used to determine the parameters of group contribution thermodynamic models. The predictive capacities of the equations obtained were shown to be quite precise (8% mean deviation).

SCOPE

The optimization of many industrial processes is partially based on reliable thermodynamic data. For example, in the food industry the knowledge of activity coefficients of aroma compounds in the different substrates encountered in food is of particular interest if processes are to be improved and good quality-price levels are to be obtained.

Several authors have taken measurements based on static methods that permit the determination of these data in model systems (Buttery et al., 1971; Voilley et al., 1977; Kieckbusch and King, 1979). Sorrentino et al. (1983) gave a critical evaluation of these methods. A dynamic method, which was recently developed by Leroi et al. (1979), was successfully used for slightly viscous model food systems by Lebert and Richon (1984a, b). A new cell was recently designed by Richon et al., (1985) to work with highly viscous and/or foaming mixtures and to study the influence of solvent molecular sizes (molecular weight and chain length) on activity coefficients of volatile components.

Numerous measurements of activity coefficients have been performed for solutes differing in chemical nature (alcohols, aldehydes, ketones, and esters), and at infinite dilution in different polyethylene glycols and glucose syrups.

Comparisons between predicted values from two group-contribution thermodynamic models and our experimental results show the ASOG model (Derr and Deal, 1968) is better than the UNIFAC model (Fredenslund et al., 1975), but not accurate enough. In this work, new group-contribution parameters have been adjusted and proposed for the ASOG model.

CONCLUSIONS AND SIGNIFICANCE

The inert gas stripping method, which is very suitable to perform accurate measurements of infinite dilution activity coefficients in highly viscous (1,000 mPa · s) and foaming systems, has been used to study influences of solvent characteristics. In the first step, we determined the influence of solvent molecular weight on solute activity coefficients. All the solute activity coefficient values increase as a function of polyholoside concentrations in water-polyholoside systems, but the amplitude of the effects becomes lower as the polyholoside molecular weight increases. It was shown that experimental results could be used as a data base for the estimation of group-contribution parameters of thermodynamic models. It is then possi-

ble to estimate useful values when no experimental data are available. In this work, the predictive capacities of the ASOG model used with our new adjusted group-contribution parameters were tested on our experimental results and were found very precise, with less than 8% mean deviation.

Materials and Methods

The characteristics and origin of the volatile components are presented in Table 1. The substrates are described in Table 2. For polyholosides, the mean molecular weight was determined by a freezing point depression method.

The experimental method applied here has been described in previous papers (Leroi et al., 1977, Richon and Renon, 1980) and the cell used has been described in the paper by Richon et al. (1985). The equilibrium cell "dilutor cell" was composed of a glass tube closed at each end by plugs. At the lower end of the glass tube is found the carrier gas inlet holding the capillary injectors. At the other end is the vapor phase outlet. A known amount of substrate was introduced into the cell. The solute (about 50 μL) was injected directly into the cell (its mole fraction was always less than 5×10^{-4}), which was connected to the chromatographic circuit. Samples of vapor phases flowing out continuously from the cell were periodically analyzed by gas-liquid chromatography. This allowed the calculation of the infinite

Table 1. Characteristics of Volatiles

Name	Source	Min. Purity*	p^s Pa × 10^3 (T)**
Methanol	Merck	99.7	21.8 (a)
Methanol	↓	↓	16.9 (b)
Ethanol	Merck	99.85	10.5 (a)
Ethanol	↓	↓	7.8 (b)
n-Propanol	Merck	99.7	3.8 (a)
n-Propanol	↓	↓	2.7 (b)
2-Propanone	Merck	99.0	38.0 (a)
Butanone	Merck	99.5	15.2 (a)
Ethyl formate	Merck	97.0	40.7 (a)
Ethyl acetate	Merck	99.7	16.0 (a)
Propyl acetate	Eastman Kodak	99.0	3.8 (a)
Ethanal	Merck	99.0	146.6 (a)
Propanal	Carlo Erba	99.0	58.6 (a)

*Purity expressed as wt. % of volatiles contained in commercial product.
** (T): (a) at 303.15 K; (b) at 298.15 K

Table 2. Characteristics of Substrates

Name*	Source	Molecular Weight
PEG 6,000	Merck	5,000–7,000
PEG 10,000	Merck	8,500–11,500
PEG 35,000	Merck	—
Glucose DE 100	Merck	180
Maltose DE 50 (monohydrate)	Merck	360
Glucose syrup DE 61.5	Roquette	324**
Glucose syrup DE 20	Roquette	1,170**

*PEG: Polyethylene glycol.
DE: Dextrose equivalent, g glucose/100 g dry matter.
**Mean values were determined by the freezing point depression method.

Table 3. Activity Coefficients γ^∞ of Volatiles in Water and Water-Sugar Systems

		Substrate, Weight Fraction							
		Glucose DE 100		Maltose DE 50		Glucose Syrups			
						DE 61.5 (2)		DE 20 (2)	
Volatiles	Pure Water	0.15	0.50	0.15	0.50	0.15	0.50	0.15	0.50
				T = 298.15 K					
Methanol	1.64	1.94*	2.39*	1.71*	1.93*	1.77	1.93	1.74	2.01
Ethanol	3.55	4.32*	5.85*	3.8*	4.38*	3.93	4.81	3.82	4.41
n-Propanol	11.2	13.4*	19.4*	12.2*	13.8*	12.1	15.1	11.6	13.4
				T = 303.15 K					
2-Propanone	7.7	9.9*	14.7*	9.2*	11.7*	9.2	12.1	8.9	10.9
Butanone	29.5	34.5*	60.4*	35.5*	46.0*	34.9	46.7	31.7	36.5
Ethyl formate	59.0	76.0	112.0	74.0	108.0	75.0	113.0	69.0	91.0
Ethyl acetate	77.0	108.0*	180.0*	106.0*	170.0*	110.0	184.0	95.0	136.0
Propyl acetate	450.0	670.0*	1,150.0*	610.0*	970.0*	650.0	1,000.0	530.0	680.0
Ethanal	4.43	4.9*	5.95*	4.8*	5.3*	4.9	5.9	4.85	5.35
Propanal	15.6	16.8*	22.2*	16.7*	19.0*	17.7	21.7	16.6	18.8

*Data used for parameter adjustment
DE: Dextrose equivalent
(2): Double glucose

Table 4. Henry's Constants H^∞ in Water and Activity Coefficients γ^∞ of Volatiles in Water-Polyethylene Glycol (PEG) Systems

		γ^∞: Substrate, Weight Fraction						
	H^∞		PEG 6,000		PEG 10,000		PEG 35,000	
Volatiles	Pure Water	Pure Water	0.15	0.30	0.15	0.30	0.15	0.30
			$T = 298.15$ K					
Methanol	0.27	1.64	1.65*	1.61*	1.62	1.63	1.62	1.6
Ethanol	0.28	3.55	3.56*	3.38*	3.5	3.4	3.57	3.45
n-Propanol	0.30	11.20	9.9*	8.8*	10.1	9.1	11.0	9.9
			$T = 303.15$ K					
2-Propanone	2.94	7.70	8.2*	8.7*	8.2	8.4	8.1	8.4
Butanone	4.50	29.50	28.0*	25.0*	28.9	26.4	29.6	28.6
Ethyl formate	23.4	59.0	68.0	73.0	64.0	69.0	67.6	74.5
Ethyl acetate	12.6	77.0	85.5*	94.3*	87.0	92.0	89.0	99.0
Propyl acetate	17.6	450.0	460.0*	450.0*	450.0	440.0	480.0	515.0
Ethanal	6.60	4.43	5.3*	6.0*	5.4	6.1	5.2	6.0
Propanal	9.0	15.30	16.9*	17.7*	17.6	18.6	18.0	20.4

*Data used for parameter adjustment.

dilution activity coefficients from the expression:

$$\gamma_i^\infty = \left(-\frac{1}{t}\ln\frac{S_i}{(S_i)_{t=0}}\right)\frac{n_s RT}{VP_{i(T)}^s} \qquad (1)$$

This expression is derived from equilibrium and mass balance equations. V is the volumetric flow rate of inert gas and n_s is the total number of moles of water and dissolved solids. S_i is the chromatographic peak area of solute at a time t and P_i^s is the saturating vapor pressure of solute, i, at temperature T.

Results and Discussion

Experimental determination of γ^∞

Henry's constants and activity coefficients are presented in Tables 3 and 4. Deviations from Raoult's law are positive and quite large in all chemical series. For a homologous series, the activity coefficients increase with the number of carbon atoms. This confirms the results of Lebert and Richon (1984a, b) and is probably due to the decrease of the solute polarity as the chain length increases.

Mixtures Containing Carbohydrates. In the presence of sugars, activity coefficients of all the volatiles studied became higher than those observed in pure water. The behavior of vola-

Table 5. Comparison of Experimental and ASOG and UNIFAC Predicted Activity Coefficient Values γ

		Prediction, calculated with			
		ASOG Parameters*		UNIFAC Parameters**	
Volatiles	Exp. γ	γ	Error %	γ	Error %
Methanol	1.64	1.57	−4.26	2.24	+36.6
Ethanol	3.55	4.44	+25	6.15	+73
Propanol	11.2	14.1	+25	29.1	+159
2-Propanone	7.7	16.3	+111	18.4	+138
Butanone	29.5	52.4	+77.6	83.9	+184
Ethyl formate	59.0	17.3	−70	—	—
Ethyl acetate	77.0	55.8	−38	35	−54
Propyl acetate	450.0	188.0	−58	163	−63
Ethanal	4.43	11.1	+150	41	+825
Propanal	15.6	44.6	+185	189	+1,111

Mean error: ASOG, 76%; UNIFAC, 260%

*Kojima and Toschigi (1979)

**Fredenslund et al. (1975)

Table 6. New Parameters for ASOG Model

$A_n k \rightarrow k$ ↓ n	Water	CH_2	OH	C = 0	COO	CHO	Glucose	Double Glucose	Ethylene Glycol
Water	1	−0.747	0.545	0.956	0.913	0.891	0.701	0.701	0.699
CH_2	0.828	1	0.396	1.493	3.072	1.267	0.770	0.739	0.416
OH	1.876	0.088	1	*	*	*	−0.102	−1.086	−1.092
C = O	1.492	1.104	*	1	*	*	−0.199	1.019	0.484
COO	2.061	2.378	*	*	1	*	2.343	2.143	3.230
CHO	0.904	0.846	*	*	*	1	0.275	1.253	−1.056
Glucose	0.714	0.350	0.649	1.802	0.660	1.411	1	*	*
Double glucose	0.714	0.554	1.927	0.883	0.683	0.483	*	1	*
Ethylene glycol	0.710	1.343	1.524	1.250	0.344	2.701	*	*	1

*Undetermined value

tile components in these systems seems to be the same as that in aqueous salts solutions (salting-out effect). The activity coefficients are a linear function of the sugar weight fractions, but the slopes depend on the particular volatile compound considered, even in a homologous series.

At the same sugar weight fractions, activity coefficients of volatile components decrease as the molecular weight of substrates increases. With very high molecular weight carbohydrates [starch, low dextrose equivalent (DE) glucose syrups] these activity coefficients would probably become the same or lower than those observed in pure water, as shown by Lebert and Richon (1984). This is explained by the helical structure of polymers, which can lead to entrapment of volatile components.

Mixtures Containing Polyethylene-Glycols. In general, the effect of polyethylene-glycol (PEG) content on the activity coefficients of volatiles in the mixture is much lower than that for sugar. The variations of activity coefficients with an increase of PEG concentrations or molecular weight (at the same weight fractions) are within experimental error and thus definite conclusions could not be advanced.

Representation by thermodynamic models

As a preliminary study, we calculated infinite dilution activity coefficients of volatile components in the volatile/water binary mixtures with ASOG and UNIFAC equations using parameter tables from Kojima and Tochigi (1979) and Fredenslund et al. (1975). The results (Error = γ model − γ experimental/γ experimental) are given in Table 5.

We may note that the ASOG model predicts data that are in the best agreement with measurements. Thus, the ASOG model was retained for this study, and a new set of parameters was determined for the groups which were involved in the molecules we studied. For this purpose, experimental data were separated in two groups:

1. Data for systems containing low molecular weight substrates, whose structure was in agreement with the hypothesis of solutions-of-groups models, were used as a data base for the estimation of the parameters. These systems are indicated with an asterisk in Table 3.
2. Other values, used later to test the predictive capabilities of the resulting equation.

The procedure for estimating parameters was based on a modified simplex algorithm (Fredenslund et al., 1975). The resulting values are represented in Table 6.

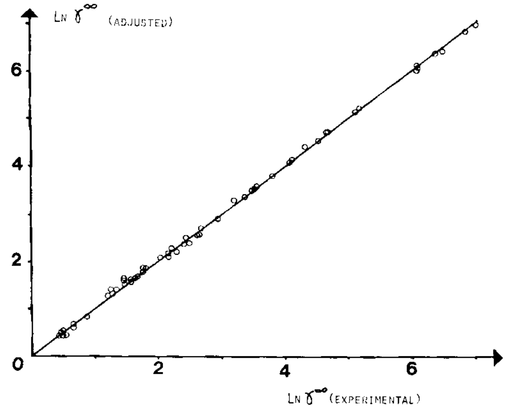

Figure 1. Comparison between calculated data, corresponding to the systems involved in adjustment, and experimental values of ln γ_i^{∞}.
Each O represents one volatile i in a system.

Table 7. Results of ASOG Model Parameters Fitting for Water/Volatiles Systems

Volatiles	γ Exp.	γ ASOG Model*	Error Percent
Methanol	1.64	1.62	− 0.6
Ethanol	3.55	4.08	+ 15.0
n-Propanol	11.2	10.7	− 4.5
2-Propanone	7.7	8.0	+ 4.0
Butanone	29.5	28.9	− 2.0
Ethyl formate	59.0	12.2	− 79.0
Ethyl acetate	77.0	81.0	+ 5.2
Propyl acetate	450.0	430.0	− 4.4
Ethanal	4.43	4.54	+ 2.5
Propanal	15.6	15.9	+ 2.0

Mean error (absolute): 11.9%
*Parameters in Table 6

Figure 1, representing the plot of fitted vs. experimental values of activity coefficients, shows that the flexibility of the ASOG model is sufficient for the representation of the behavior of our systems (4% mean deviation). However, as can be seen in Table 5, the representation of volatile chain length is not always good, especially for alcohols and esters. For these two series, represented by three compounds each, constraints on the parameters of the model are higher than for the other series, represented by only two compounds. These difficulties in chain length representation are related to the combinatorial part of the model. The necessary hypothesis for the calculation of entropic effects does not seem to be consistent with the complex structure of the water/organic mixtures.

Using this new set of parameters it is possible to predict values of activity coefficients for the systems not used in the parameter adjustment calculations, Tables 7 and 8.

Figure 2 represents a plot of predicted vs. experimental values. It shows that the predictive ability of the ASOG model is

Table 8. Prediction of Activity Coefficients γ^{∞} of Volatiles in Water-Sugar Systems

	Substrate, Weight Fraction			
	Glucose syrups			
	DE 62.5		DE 20	
Volatiles	0.15	0.50	0.15	0.50
	$T = 298.15$ K			
Methanol	1.64	1.93	1.57	1.86
Ethanol	4.27	5.11	4.09	4.91
n-Propanol	11.6	14.1	11.1	16.0
	$T = 303.15$ K			
2-Propanone	9.4	12.3	9.7	12.5
Butanone	35.1	46.1	36.0	46.8
Ethyl formate	75	113.0	69.0	91.0
Ethyl acetate	101.0	167.0	102.0	172.0
Propyl acetate	540.0	910	545	935
Ethanal	4.9	5.2	5.0	5.3
Propanal	18.0	19.2	18.2	19.5

DE: Dextrose equivalent

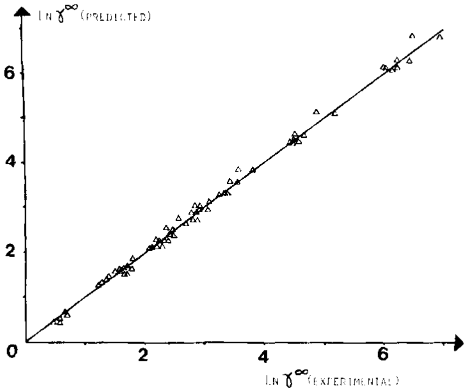

Figure 2. Comparison between calculated data for all systems and experimental values of ln γ_i^∞.
Each Δ represents one volatile *i* in a system.

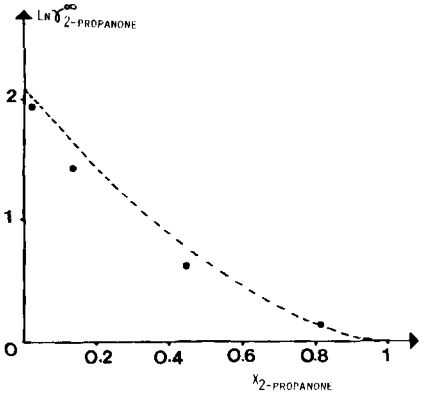

Figure 3. Logarithm of activity coefficients of 2-propanone in water.
---- predicted values (ASOG with parameters of Table 6) ● experimental values

quite good for systems of the same type (but with higher molecular weight substrates) as those used for parameter estimation: 8% mean deviation for water/glucose system predictions using water/glucose and water/maltose data for parameter estimation. A comparison of Tables 3 and 7 shows that there is a large difference between the accuracy of a prediction for a glucose syrup DE 20 (12%) and that for a glucose syrup DE 61.5 (4%). This is due to the use of low molecular weight sugars (glucose and maltose) for glucose group parameter estimations and also to the assumption that single-bonded and double-bonded monomers have the same behavior. The high error of predictions for DE 20 (concerned mainly with double-bonded monomers) indicates that glucose monomers must be differentiated. However the quality of predictions is sufficient considering the number of data points used in the adjustment procedure and the range of molar fractions within which the predictions are possible. Figure 3 shows an example of long-range extrapolation: finite dilution data from parameters estimated with infinite dilution experimental points.

Acknowledgment

The authors are grateful to H. Renon from the Ecole des Mines de Paris and D. Simatos from the ENS.BANA for their interest in this study. This work was performed with financial support from the French Government: D.D.S.T.I., aid. 83C 01 66.

Notation

A = UNIFAC interaction parameter, temperature-independent
a = activity
l = UNIFAC geometry parameter
n = number of atoms other than hydrogen
n_s = number of moles of solvent
P = vapor pressure
Q = UNIFAC geometric parameter
q = UNIFAC geometric parameter
R = gas constant
R_K = UNIFAC geometric parameter
S = peak area, arbitrary units
r = UNIFAC geometric parameter
t = time
T = temperature, K
v = UNIFAC geometric parameter
w = weight fraction
X = group fraction
x = mole fraction
Z = UNIFAC coordination number

Greek letters

γ = activity coefficient
Γ = group activity coefficient
ϕ = UNIFAC geometric parameter
θ = UNIFAC geometric parameter
ν = number of groups
ψ = ASOG interaction parameter, temperature-dependent

Subscripts

i, j = molecules i or j
K, n, m, P = groups K, n, m, or P
Δ = solvent
w = water

Superscripts

C = combinatorial term
(i) = molecule i in a pure state
i = molecule i
R = residual term
s = saturating value

Appendix

Solutions-of-group methods require experimental data from phase equilibria in order to determine a set of parameters to be used to predict the behavior of molecules formed by the same groups as those included in the data base. These methods are based on empirical hypothesis set forth by Wilson and Deal (1962):

1. The logarithm of the activity coefficient is the sum of two terms: a combinatorial term induced by molecule differences in size and shape, and a second term obtained from interactions, referred to as the residual term:

$$\ln_i = \ln \gamma_i^R + \ln \gamma_i^c \tag{A1}$$

2. The residual term should be the sum of the individual contributions of each group in the mixture minus the individual contributions group in pure molecules:

$$\ln \gamma_i^R = \sum_K \nu_K^{(i)} (\ln \Gamma_K - \ln \Gamma_K^{(i)}) \tag{A2}$$

where

Γ_K = activity coefficient of group K in the mixture

$\Gamma_K^{(i)}$ = activity coefficient of group K in pure i

$\nu_K^{(i)}$ = number of groups of type K in molecule i.

3. Γ_K at a given temperature is only a function of the concentration of the different groups; it is independent of the group distributions in the different molecules.

$$\Gamma_K = F(X_1, X_2, \ldots, X_K) \qquad \text{(A3)}$$

with X_K being the mole fraction of group K:

$$X_K = \frac{\sum_i \nu_K^{(i)} x_i}{\sum_j \sum_i \nu_j^{(i)} x_i} \qquad \text{(A4)}$$

where x_i is the mole fraction of molecule i.

On this basis, one could obtain a group contribution model by specifying:

- The equation giving γ_i^c
- The definition of the different groups
- The form of the function Γ_K

The ASOG model uses these following equations:

$$\ln \gamma_i^c = \ln \frac{n_i}{\sum_j n_j x_j} + 1 - \frac{n_i}{\sum_j n_j x_j} \qquad \text{(A5)}$$

$$\ln \Gamma_K = -\ln \sum_P X_P \psi_{K,P} + 1 - \sum_P \frac{X_P \psi_{P,K}}{\sum_m X_m \psi_{P,m}} \qquad \text{(A6)}$$

where n_j = the number of atoms other than hydrogen in molecule j, and $\psi_{P,K}$ = the interaction parameter between groups P and K.

The UNIFAC model is defined by:

$$\ln \gamma_i^c = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + P_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \qquad \text{(A7)}$$

$$P_i = \frac{Z}{2}(r_i - q_i) - (r_i - l) \quad \text{and} \quad Z = 10 \qquad \text{(A8)}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \phi_i = \frac{v_i x_i}{\sum_j v_j x_j} \qquad \text{(A9)}$$

where

$$v_i = \sum_K \nu_K^i R_K \qquad q_i = \sum_K \nu_K^i Q_K$$

R_K and Q_K are geometrical parameters deducible from Bondi (1968).

$$\ln \Gamma_K = Q_K \left[1 - \ln \left(\sum_m \theta_m \psi_{m,K} \right) - \sum_m \left(\theta_m \psi_{K,m} \Big/ \sum_n \theta_n \psi_{n,m} \right) \right] \qquad \text{(A10)}$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad \text{(A11)}$$

$$\psi_{n,m} = \exp(-A_{n,m}/T) \qquad \text{(A12)}$$

$A_{n,m}$ is an interaction parameter between groups n and m ($A_{n,m} \neq A_{m,n}$).

Literature cited

Bondi, A., *Physical Properties of Molecular Crystals Liquids and Gases*, Wiley, New York (1968).

Buttery, R. G., J. L. Bomben, D. G. Guadagni, and L. C. Ling, "Some Considerations on the Volatilities of Organic Flavor Compounds in Foods," *J. Agr. Food Chem.*, **19**(6), 1045 (1971).

Derr, E. L., and C. H. Deal, "Analytical Solution of Groups: Correlation of Activity Coefficients through Structural Group Parameters," *I. Chem. E. Symp. Ser.*, **32**, 40 (1968).

Fredenslund, A., R. K. Jones, and J. M. Prausnitz, "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures," *AIChE J.*, **21**(6), 1086 (1975).

Kieckbusch, T. G., and C. J. King, "Partition Coefficients for Acetates in Food Systems," *J. Agr. Food Chem.*, **27**, 504 (1979).

Kojima, K., and K. Tochigi, *Prediction of Vapor-Liquid Equilibria by the ASOG Method*, Elsevier, New York (1979).

Lebert, A., and D. Richon, "Study in the Influence of Solute (*n*-Alcohols and *n*-Alkanes) Chain Length on Their Retention by Purified Olive Oil," *J. Food Sci.*, **49**(5), 1301 (1984a).

———, "Infinite Dilution Activity Coefficients of *n*-Alcohols as a Function of Carbohydrates Concentration in Water-Carbohydrates Systems," *J. Agr. Food Chem.*, **32**, 1156 (1984b).

Leroi, J. C., J. C. Masson, H. Renon, J. F. Fabries, and H. Sannier, "Accurate Measurement of Activity Coefficients at Infinite Dilution by Inert Gas Stripping and Gas Chromatography," *Ind. Eng. Chem. Process Des. Dev.*, **16**(1), 139 (1979).

Richon, D., and H. Renon, "Infinite-Dilution Henry's Constants of Light Hydrocarbons in *n*-Hexadecane, *n*-Octadecane, and 2,2,4,4,6,8,8 Heptamethylnonane by Inert Gas Stripping, *J. Chem. Eng. Data*, **25**, 59 (1980).

Richon, D., F. Sorrentino, and A. Voilley, "Infinite-Dilution Activity Coefficients by Inert Gas Stripping Method: Extension to the Study of Viscous and Foaming Mixtures, *Ind. Eng. Chem. Process Des. Dev.*, **24**, 1160 (1985).

Sorrentino, F., D. Richon, and A. Voilley, "Mesure de la Volatilité de Substances d'arôme à l'aide de Deux Techniques," *Science des Aliments*, **4**(III), 105 (1983).

Voilley, A., D. Simatos, and M. Loncin, "Gas Phase Concentration of Volatiles in Equilibrium with a Liquid Aqueous Phase," *Lebens. Wiss. u. Techno.*, **10**, 45 (1977).

Wilson, G. M., and C. H. Deal, "Activity Coefficients and Molecular Structure," *Ind. Eng. Chem. Fundam.*, **1**(1), 20 (1962).

Manuscript received April 1, 1985, and revision received April 14, 1986.