h	constant in eq 1
I	moment of inertia of the suspension system, g-cm^2
L	distance of the scale from the mirror, cm
M_i, M_j	molecular weights
R	radius of the disk, cm
T_{p_0}	period of oscillation of the disk under vacuum, s
x_1, x_2, x_3	molar fractions of vapors in the mixture
β	dimensionless harmonic mean separation, b/δ
δ	boundary layer thickness, cm
Δ_0	damping decrement under vacuum
Δ	damping decrement in the gas
μ, μ_1, μ_2, μ_3	dynamic viscosity, μP
ρ	density of the fluid, g/cm^3
θ	ratio of periods of oscillation in the gas and in vacuum, T_1/T_{p_0}
ϕ_{12}, ϕ_{13}, ϕ_{21}, ϕ_{23}, ϕ_{31}, ϕ_{32}	constants in eq 4

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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

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The inert gas stripping method described in previous papers has been extended to accurate measurements of Henry's constants. The results show the very strong influence of branching of the molecule of solvent on solubility. Determinations of limiting Henry's constants were carried out for C_1 to C_4 hydrocarbons in *n*-hexadecane and 2,2,4,4,6,8,8-heptamethylnonane at 298.15 K and in *n*-octadecane at 323.15 K. Comparisons of results in *n*-hexadecane and *n*-octadecane are made with published results.

Solubilities of gases characterized by Henry's constants are useful data for oil recovery or transportation problems.

Oil is a complex mixture of many hydrocarbons. Among them are normal or branched molecules. Effect of branching is very important on most thermodynamical properties. It must be carefully investigated. The results of the present investigation show that the solubility of light hydrocarbons is several times greater in branched than in normal hexadecane.

A fast and accurate method is required to investigate numerous solvents. For this purpose, the gas stripping method is particularly convenient but a special equilibrium cell should be used.

Chemicals

Methane, ethane, *n*-propane, and *n*-butane were supplied by L'Air Liquide, the stated purities are respectively 99.95, 99.9, 99.5, and 99%. *n*-Hexadecane was obtained from Merck, *n*-octadecane from Fluka, and 2,2,4,4,6,8,8-heptamethylnonane from Sigma. These three components have a purity of not less than 99% and have been used without further purification.

Apparatus and Procedure

The apparatus and procedure were described in a previous paper (*4*, *6*). Only one part of the apparatus, the equilibrium cell, is changed. The new cell appears on Figure 1. The volume of vapor phase, V_G, above liquid mixture in the cell has been reduced as suggested by Richon et al. (*6*) and the collector has been modified to obtain a simple geometrical shape for the vapor space. The liquid level in the cell should be not lower than 1 cm from the top of the cell. As a consequence, it is necessary to place two baffles in the glass cell body to achieve efficient stirring of liquid phase. Equilibrium between liquid and vapor phase is reached only with these special conditions of cell design. Several parameters such as length and number of capillaries, position of baffles, and speed of magnetic stirring have been investigated.

Henry's constant is given by the equation

$$H_i^{\infty} = -\frac{1}{t}\ln\frac{S_i}{(S_i)_{t=0}}\,\frac{RTN}{D + \dfrac{V_G}{t}\ln\dfrac{S_i}{(S_i)_{t=0}}}$$

It is a simplification of Duhem and Vidal's (*2*) equation when the corrective term accounting for the variation of the total gas flow rate due to the vaporization of solute is neglected.

Results and Discussion

Measurements for methane to *n*-butane in *n*-hexadecane and *n*-octadecane have been performed in order to test the new apparatus, while new Henry's constants of the new solvent 2,2,4,4,6,8,8-heptamethylnonane give information on the branching effect of the solvent in solute–solvent interaction. The results are reported in Table I.

For both *n*-hexadecane and *n*-octadecane, Henry's constants of methane obtained by gas stripping are lower than those obtained by the chromatographic retention time method (*3*, *7*) while Henry's constants of ethane to *n*-butane are in good agreement. In order to explain the discrepancy between the two methods, especially for methane, we compared our results to those of Cukor (*1*) obtained by the static method. Henry's constants of Cukor interpolated at 298.15 K are approximately

Table I. Limiting Henry's Constants of Methane to *n*-Butane in *n*-Hexadecane and 2,2,4,4,6,8,8-Heptamethylnonane at 298.15 K and *n*-Octadecane at 323.15 K

solvent	solute	temp, K	H_∞,[e] atm	H_∞,[a] atm (GLC)	H_∞,[b] atm (static)	H_∞,[c] atm (GLC)	H_∞,[d] atm (static)
n-hexadecane	methane	298.15	171.2	209	170		
n-hexadecane	ethane	298.15	27.3	26.4	27		
n-hexadecane	propane	298.15	7.45	7.41			
n-hexadecane	*n*-butane	298.15	2.01	2.02			
n-octadecane	methane	323.15	196.9			239	180
n-octadecane	ethane	323.15	35.0			33.5	
n-octadecane	propane	323.15	11.3			10.7	
n-octadecane	*n*-butane	323.15	3.72				
2,2,4,4,6,8,8-heptamethylnonane	methane	298.15	32.8				
2,2,4,4,6,8,8-heptamethylnonane	ethane	298.15	6.71				
2,2,4,4,6,8,8-heptamethylnonane	propane	298.15	2.01				
2,2,4,4,6,8,8-heptamethylnonane	*n*-butane	298.15	0.56_6				

[a] Reference 3. [b] Reference 1. [c] Reference 7. [d] Reference 8. [e] This work.

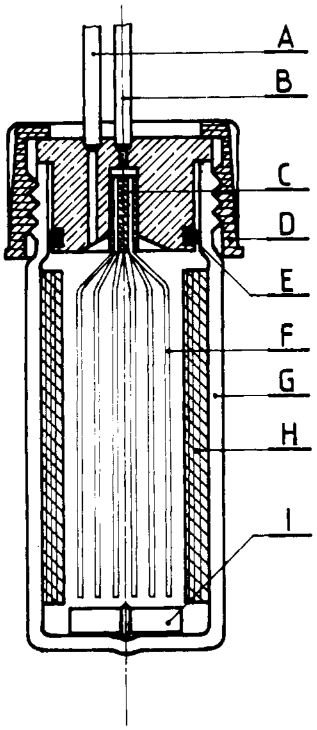

Figure 1. Equilibrium cell: A, vapor-phase outlet; B, inert gas inlet; C, Teflon seal; D, plug; F, capillaries; G, glass still body; H, baffles; I, magnetic stirrer.

equal to ours. Stepanova reports a value of 180 atm for methane, from vapor–liquid equilibria measurement. Sai Ng et al. (*7*), who report the only chromatographic measurements available on *n*-octadecane, state that estimated uncertainties for Henry's constants are about 3–5%, except for methane where it is considerably larger.

Henry's constants values for light hydrocarbons in 2,2,4,4,6,8,8-heptamethylnonane are considerably lower than those in *n*-hexadecane revealing a critical effect of branching. Patterson et al. (*9*) offer an explanation by the effect of correlation of molecular orientations in *n*-hexadecane. The destruction of order present when mixing a globular molecule to *n*-hexadecane does not exist when mixing it with branched hexadecane. Patterson and Barbe (*5*) did not find significant difference in activity coefficient or excess Gibbs energy when mixing, for example, *n*-hexane to linear and branched hexadecanes because, in this case, there is enthalpy–entropy compensation. But, when the globular molecule is very small, it seems that enthalpy–entropy compensation is not complete. The ratio of Henry's constants of light hydrocarbons in *n*-hexadecane to that in branched hexadecane decreases when carbon number increases (5.2 for methane to 3.5 for *n*-butane).

Glossary

D	carrier gas flow at pressure P and temperature T, cm^3/min
H_i^∞	Henry's constant of solute i at infinite dilution, atm
N	amount of solvent in the still, mol
R	gas constant, cm^3 atm g-mol^{-1} K^{-1}
S_i	solute i chromatographic peak area, arbitrary unit
t	time, min
T	temperature, K
V_G	volume of vapor phase in dilutor still up to sampling valve, cm^3

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