Vapor-Liquid Equilibrium Constants at Infinite Dilution Determined by a Gas Stripping Method: Ethane, Propane, n-Butane, n-Pentane in the Methane-n-Decane System

A new apparatus to measure partition coefficients K_s^∞ at infinite dilution up to 200 10^5 Pa and 423 K is described. Measurements of the systems: (1) methane-ethane-n-decane and methane-propane-n-decane at 294.25 K; and (2) methane-n-butane-n-decane at 344.25 K illustrate the reproducibility and good agreement with literature data. In addition, new data were obtained for the system methane-n-pentane-n-decane at 344.25 K up to 101 10^5 Pa.

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SCOPE

Vapor-liquid distribution ratio of light hydrocarbons between a gas phase made of methane and a liquid phase composed of heavy hydrocarbons are needed in industrial applications, for instance pipe line design or tertiary oil recovery using a miscible gas. For infinitely diluted light hydrocarbons, determination of partition coefficients, K_s^∞, can be performed using a static apparatus (Reamer et al., 1949) or retention time in gas-liquid chromatography using CH_4 as carrier gas and the heavy component as stationary phase (Stalkup and Kobayashi, 1963a; Koonce and Kobayashi, 1964).

The new method introduced in this paper consists of stripping the solute by a constant flow of gas from a solution contained in one vessel. The solution (mainly heavy hydrocarbons) and the gas (mostly CH_4 in this paper) have the composition corresponding to the equilibrium in the conditions of pressure and temperature of the measurement. The distribution ratio of the very diluted solute is related to the decrease in time of the concentration of the solute in the gas phase after stripping as determined by gas chromatography. This new technique is an extension to higher pressures of the method described by Leroi et al. (1977) and Richon et al. (1980). It uses a saturator for the gas stream entering the stripping cell.

CONCLUSIONS AND SIGNIFICANCE

A new apparatus for measuring partition coefficients of infinitely diluted solutes in mixed solvent (gas dissolved in heavy components) has been designed, constructed and tested. Tests mixtures have been used to check the reliability of measurements. The results show a good agreement with the literature data. The experimental error on K_s^∞ measurements is estimated at less than 2%.

The method is fast and may be used for studying several solutes simultaneously if all solute chromatographic peaks can be resolved. Accurate measurements are possible even for volatile solvents. Such measurements are impossible with a retention time chromatographic method. The accuracy is better than in the static methods.

INTRODUCTION

The elution method described by Leroi et al. (1977) is very suitable to measure activity coefficients at low pressures. The method was improved by Richon et al. (1980) and extended to the determination of Henry's constants at infinite dilution and atmospheric pressures (Richon and Renon, 1980). It is extended in this work to the measurement of partition coefficients in multicomponent systems where two components are at finite concentration.

EXPERIMENTAL METHOD

A constant flow of the pure gaseous component is bubbled successively in two equilibrium cells. The first cell, the saturator, contains the high boiling liquid component. The vapor-liquid equilibrium is reached in this first cell at controlled conditions of pressure and temperature. The second cell, the dilutor, is also kept at fixed conditions of pressure and temperature, but it contains the solutes to be stripped from the liquid by the gas flow. The concentration of solute in the dilutor varies with time but equilibrium is reached at all time between the outcoming vapor flow and the well-mixed liquid phase. The vapor flow is afterwards expanded

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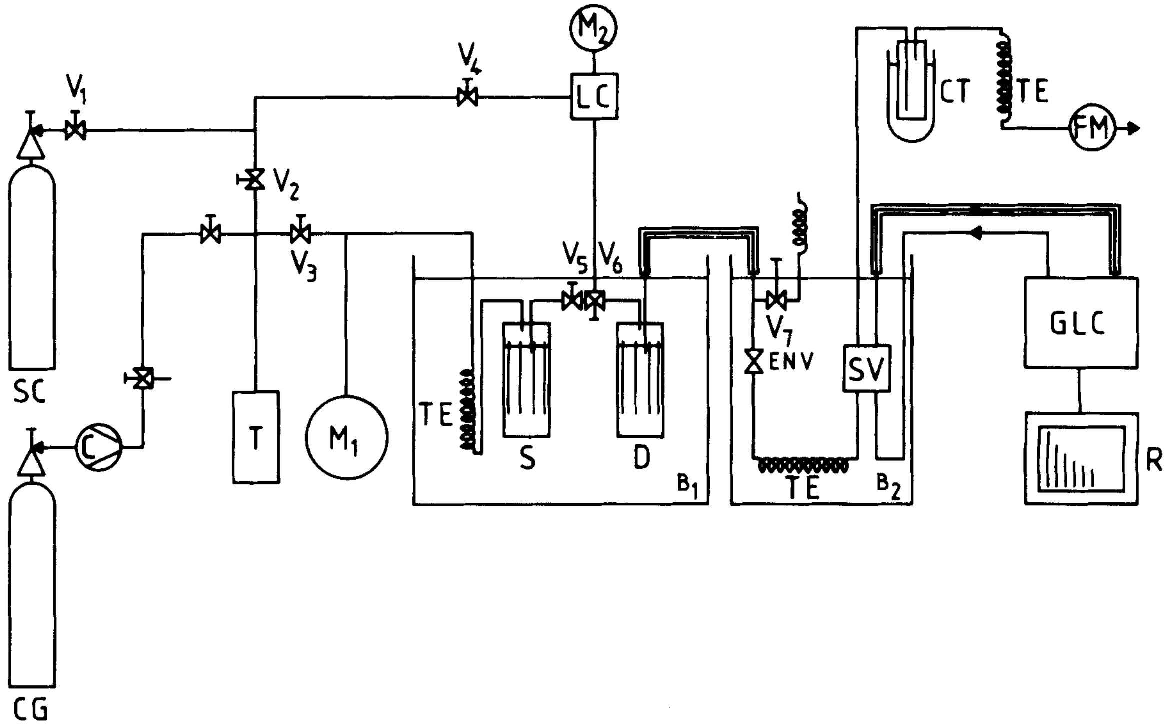

Figure 1. General set-up of the apparatus. B_1,B_2 = thermostated baths; C = compressor; CG = carrier gas cylinder; CT = cold trap; D = dilutor; ENV = expansion needle valve; FM = flow meter; GLC = gas liquid chromatograph; LC = loading cell; M_1,M_2 = manometers; R = recorder; S = saturator; SC = solute cylinder; SV = sampling valve; T = tank; TE = thermal exchanger; V = shutoff valves; V_3 = double-stage pressure regulator.

through a needle valve and sampled at time intervals in a six-way gas sampling valve connected to a gas chromatograph.

In the linearity range of the detector, the solute peak areas are exponentially decreasing functions of time. It will be shown that the limiting partition coefficient of the solute can be simply derived from the determination of this exponential curve. No calibration is necessary, there is no need to know precisely the initial concentration of solute in the liquid phase.

The method is suitable for multicomponent systems where the high boiling liquid phase is a mixture and many solutes are simultaneously stripped. The only restriction on the technique is a good chromatographic separation of solutes. An electronic integrator for the determination of peak areas yields accurate and reliable values of K_s^∞

EXPERIMENTAL EQUIPMENT

Figure 1 represents the flow diagram of the apparatus composed of five main parts: the equilibrium cells, saturator S and dilutor D; the vapor phase expanding ENV and sampling SV devices; the sample analyzer GLC; the control and measurement electronics; and the thermostats B_1 and B_2.

The two cells S and D are of similar construction (see Figure 2). In both, the gas flow is dispersed in the bottom of the cell by means of vertical capillaries open at the bottom of the cell. Bubbles of gas form slowly at the open lower extremity of each capillary. This system of dispersion is preferred to glass fritted discs in order to optimize mass transfer (Richon et al., 1980). In the saturator S, there are 20 capillaries of $3\ 10^{-4}$ m internal diameter, while in the dilutor D, there are 50 capillaries of 10^{-4} m internal diameter. The number of capillaries were chosen as a result of mass transfer study: time spent by each bubble in the mixture is over one second and depends on the chosen carrier gas flowrate. At each equilibrium pressure of preliminary tests, K_s^∞ determinations have been performed several times with different values of the carrier gas flowrate. That was necessary to check if vapor-liquid equilibrium was effectively reached in the saturator and dilutor. All the data reported in this paper were obtained with carrier gas flowrates lower than those used in the preliminary tests. The liquids in the equilibrium cells D and S are stirred by means of small magnets rotating in magnetic field produced by permanent magnets rotating in turbines.

The cells are immersed in an oil bath B_1 (Figure 1), the temperature of which is controlled and regulated to 10^{-2} K with a Hallikainen 1053 A electronic regulator from G.E.C. Elliot.

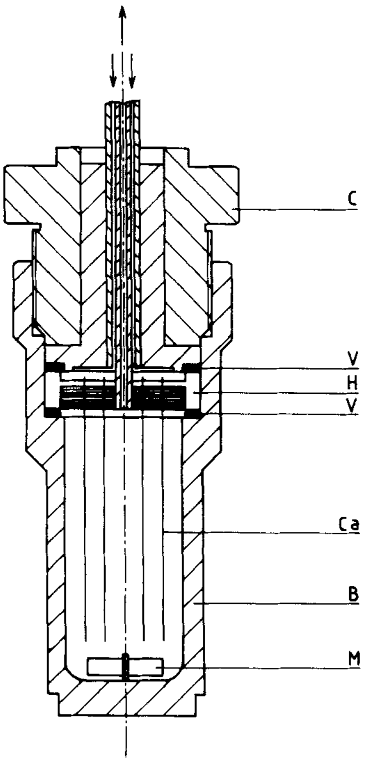

Figure 2. Dilutor. B = body; C = cap; Ca = capillaries; H = capillary holder; M = magnet; V = viton O ring.

Two circulating pumps are used to produce efficient heat transfer in the whole bath. Temperature is measured through thermocouples connected to an electronic 2100 A potentiometer from Fluke. Brooklyn mercury thermometers are used to calibrate the thermocouples with final accuracy of 0.1 K. Pressures in both cells are supposed to be identical because the pressure drops, depending on the gas flow rate, are always less than 5 10^{+3} Pa and therefore negligible. Pressure measurements are realized at the inlet of the saturator by means of a Bourdon manometer M_1 with a range of measurement 1 to 100 10^5 Pa. Accuracy on pressure readings is 0.05 10^5 Pa and is confirmed by calibration against a dead weight gauge (Budenberg, type 280 H), the accuracy of which is 0.05% of the pressure measured. This latter instrument is associated with a differential pressure null transducer and indicator (Ruska model 2413-705 and model 2416-708) of maximum sensitivity 1 Pa.

The pressure of vapor phase at the outlet of the equilibrium cell D is reduced to about 5 10^5 Pa by means of an expansion needle valve, ENV (Research Control B-2340 from Seiem). Then low-pressure vapor phase enters into a gas-sampling valve (Carle, model 2018) from which samples are periodically sent to a chromatograph (Hewlett Packard, model 5750 B). The valve V_1 (used to evacuate the apparatus at the end of an experiment), the expansion needle valve, the heat exchanger *TE*, and the gas sampling valve are immersed in an oil bath B_2, the temperature of which is kept higher than that of bath B_1 in order to avoid any condensation of either solvent or solutes. Temperature of bath B_2 is regulated within 10^{-1} K (Secasi, model minitherm) to keep the loop of the sampling valve at a constant temperature. Two heating resistances, one between B_1 and B_2 and another between B_2 and the chromatograph are also used to avoid condensation of solvent and solutes. The vapor phase at the outlet of the sampling valve is cooled in a cold trap *CT* to condensate the solvent and then heated up to room temperature in heat exchanger *TE* before entering the bubble flow meter *FM*.

EXPERIMENTAL PROCEDURE

Referring to the representation of the equipment shown in Figure 1, tank, T, is filled using compressor, C, (Nova Swiss, model 55-42121) with enough gas at high pressure provided in cylinder, *CG*. If the solute to be introduced is a gas provided in cylinder, *SC*, the cell, *LC* is filled with it; valves V_2 and V_6 are closed and V_1 and V_4 are opened allowing introduction of a small amount of the gaseous solute. Total pressure in *LC* is adjusted to a value higher than the pressure at which the equilibrium will be studied by feeding *LC* with the elution gas through valve V_2 with V_1 closed. Pressure in *LC* is read through the manometer M_2.

If the solute is a liquid, it is introduced directly into the cell, D, by means of syringe before screwing the body on the cap. Cells D and S contain about 40 cm^3 of solvent. The weight of solvent loaded is accurately determined by weighing within 10^{-4} g on an analytical balance (Mettler, model H315; maximum load, 10^3 g). The two bodies (899 g each when empty) are then screwed on their caps, S and D in this order while a small stream of eluting gas is kept flowing in order to avoid the solvent to fill up capillaries. Equilibrium pressures and flow of the eluting gas are adjusted to the required values with a two-stage regulator, V_3, and the expansion needle valve *ENV*.

If the solute is a liquid, the experiment can be started but if the solute is a gas, it is introduced through valve V_6 with V_4 and V_5 kept closed until pressure in cell, *LC*, becomes lower than in S. Then valve V_6 is closed and valve V_5 opened again. When equilibrium is reached, pressure, temperature and gas flow are constant, sampling is performed to record the curve: solute peak area vs. time. At the end of the experiment, V_3 and *ENV* are closed and depressurization is obtained by opening valve V_7. A capillary tubing at the outlet of V_7 is used to protect saturator, S, and dilutor, D, against a too fast depressurization. After each experiment the apparatus is cleaned by heating and sweeping with nitrogen gas during several hours.

INTERPRETATION OF MEASUREMENTS

From mass balances around dilutor (Figure 3 and Appendix) one can obtain:

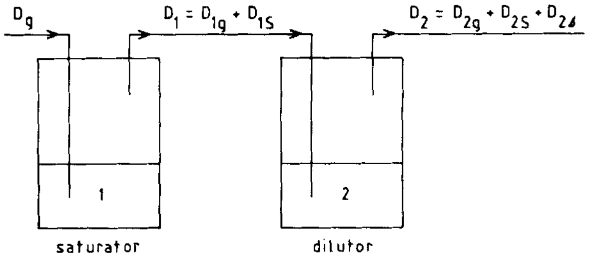

Figure 3. Overall molar balance.

$$\frac{dN_{2s}}{dt} = -y_s D_2 = D_{2s} \tag{1}$$

where y_s is mole fraction of solute in the gas flowing out of the dilutor and N_{2s} the molar hold-up of solute in the dilutor. It was assumed that the hold-up of g and S in the dilutor is constant. D_{2s} is small compared to D_{2g} and D_{2S} therefore:

$$\frac{dN_{2s}}{dt} = -\frac{y_s}{1 - y_S} D_{2g} \tag{2}$$

where y_S is the mole fraction of solvent in the dilutor. In fact, the volumetric flow rate D'_{2g} is measured at pressure P_{at} and temperature T_r after condensation of the solvent. A correction for water vapor pressure is applied if a bubble flow meter *FM* is used

$$\frac{dN_{2s}}{dt} = -\frac{y_s}{1 - y_S} \frac{D'_{2g} P_o}{Z_{go} R T_r} \tag{3}$$

where Z_{go} is the compressibility factor of the gas in these conditions, and P_o is atmospheric pressure corrected for water vapor pressure.

Among the total number of moles of solute in dilutor, N_{2s}, part is in the vapor phase as already pointed out by Duhem and Vidal (1978).

$$N_{2s} = N_2^L x_s + N_2^V y_s \tag{4}$$

where x_s is the mole fraction of solute in the liquid phase. By definition of the distribution coefficient:

$$y_s = K_s^\infty x_s \tag{5}$$

The solute mole fraction in the liquid phase x_s is small:

$$N_{2s} = x_s \left[\frac{N_{2S}^L}{1 - x_g} + \frac{PV}{ZRT} K_s^\infty \right] \tag{6}$$

eliminating x_s and y_s between Eqs. 3, 5 and 6

$$\frac{dN_{2s}}{dt} = -K_s^\infty \frac{N_{2s}}{\dfrac{N_{2S}^L}{1 - x_g} + \dfrac{PV}{ZRT} K_s^\infty} \frac{1}{1 - y_S} \frac{D'_{2g} P_o}{Z_{go} \cdot R T_r} \tag{7}$$

To use Eq. 7, it is necessary to know x_g and y_S. If not found in literature, these two data can be obtained by measuring vapor-liquid equilibria of the binary solvent-gas mixture, using a static apparatus.

Integration of Eq. 7 yields:

TABLE 1. ORIGIN AND PURITY OF THE CHEMICALS USED

Material	Origin	Purity
Methane	Air Gaz	99.995% vol.
Ethane	Air Gaz	99.95% vol.
Propane	L'Air Liquide	99.5% vol.
n-Butane	L'Air Liquide	99% vol.
n-Pentane	Merck	99% GLC
n-Decane	Fluka	≥99% GLC

TABLE 2. *K* VALUES FOR ETHANE AT INFINITE DILUTION IN THE METHANE-N-DECANE SYSTEM: $T = 294.25$ K

Pres., 10^5 Pa	$\frac{C}{B}$,* %	$K_s^{\infty a}$	$\overline{K_s^{\infty}}^a$	$\frac{C}{B}$,** %	$K_s^{\infty b}$	$\overline{K_s^{\infty}}^b$	$K_s^{\infty c}$	Δ^d, %
5.2				4.7	5.51_1		5.34	3.2
5.2				4.5	5.55_7	5.53		4.1
10.0	4.5	2.88_6		4.4	2.89_3		2.73	5.9
10.0	4.3_5	2.90_7	2.90	4.3	2.91_5	2.90		6.6
21.0_5	4.6	1.55_3		4.5	1.55_8		1.45	7.2
21.0_5	4.4	1.52_9		4.3	1.53_4			5.7
21.0_5	4.4_5	1.52_2	1.54	4.3_5	1.52_7	1.54		5.2
21.0_5	3.9	1.52_9		3.8	1.53_4			5.7
21.0_5	5.3	1.56_0		5.2	1.56_6			7.8
21.0_5	4.9	1.53_7		4.8	1.54_3			6.2
42.6	4.9	0.910_4		4.5	0.919_8		0.853	7.3
42.6	5.8	0.910_3	0.91	5.4	0.919_8	0.92		7.3
95.3	5.7	0.63_4					0.628	1.0
95.3	5.4	0.63_9	0.63_5					1.7

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[a] Value calculated with methane solubility data, x_g, and saturated liquid molar volumes, v^{SL}, from Beaudoin and Kohn (1967).

[b] Value calculated with methane solubility data, x_g, from Koonce and Kobayashi (1964) and saturated liquid molar volumes, v^{SL}, from Beaudoin and Kohn (1967).

[c] Literature data from Stalkup and Kobayashi (1963b).

[d] $\Delta = \dfrac{\dfrac{K_s^{\infty a} + K_s^{\infty b}}{2} - K_s^{\infty c}}{K_s^{\infty c}}$

* C/B = vapor-phase correction term entering in calculation of $K_s^{\infty a}$ (Eq. 11)

** C/B = vapor-phase correction term entering in calculation of $K_s^{\infty b}$ (Eq. 11)

TABLE 3. *K* VALUES FOR PROPANE AT INFINITE DILUTION IN THE METHANE-N-DECANE SYSTEM: $T = 294.25$ K

Pres., 10^5 Pa	$\frac{C}{B}$,* %	$K_s^{\infty a}$	$\overline{K_s^{\infty}}^a$	$\frac{C}{B}$, **%	$K_s^{\infty b}$	$\overline{K_s^{\infty}}^b$	$K_s^{\infty c}$	Δ^d, %	K_s^{∞},^{e}	Δ^f, %
5.2				1.6	1.53_8	1.54	1.42	8.3	1.57[†]	−2.0
5.2				1.5	1.53_4			8.0		−2.3
21.0_5	1.9_1	0.457_5		1.8_7	0.459_6			5.9		3.0
21.0_5	1.4_4	0.457_8	0.458	1.4_0	0.459_8	0.460	0.433	6.0	0.445[†]	3.1
95.3_5	1.9	0.252						0.8		
95.3_5	2.5	0.254	0.253				0.250	1.6		

For *, **, [a], [b], [c] and [d], see Table 2.

[e] Experimental data from Koonce and Kobayashi (1964).

[f] $\Delta = \dfrac{\dfrac{K_s^{\infty a} + K_s^{\infty b}}{2} - K_s^{\infty e}}{K_s^{\infty e}}$

[†] Interpolated data.

TABLE 4. *K* VALUES FOR N-BUTANE AT INFINITE DILUTION IN THE METHANE-N-DECANE SYSTEM: $T = 344.25$ K

Pres., 10^5 Pa	$\frac{C}{B}$, %*	$K_s^{\infty a}$	$\frac{C}{B}$, %**	$K_s^{\infty b}$	$K_s^{\infty c}$	Δ^d, %	$K_s^{\infty e}$	Δ^f, %
5.0			1	1.40				
21.9	1.4_3	0.388	1.4_1	0.390	0.353	10.2		
56.1	1.5_4	0.227	1.5_1	0.230	0.222[†]	2.9	0.231[†]	−1.1

For *, **, [a], [c] and [d], see Table 2.

[b] Value calculated with methane solubility data, x_g, and saturated liquid molar volumes, v^{SL}, from Reamer et al. (1942).

[e] Datum from Reamer et al. (1949).

[f] $\Delta = \dfrac{\dfrac{K_s^{\infty a} + K_s^{\infty b}}{2} - K_s^{\infty e}}{K_s^{\infty e}}$

[†] Interpolated data.

$$\log \frac{N_{2s}(t)}{N_{2s}(o)} = - \frac{K_s^{\infty} t}{\dfrac{N_{2S}^L}{1 - x_g} + \dfrac{PV}{ZRT} K_s^{\infty}} \, \frac{1}{1 - y_S} \, \frac{D'_{2g} P_o}{Z_{go} R T_r} = At \qquad (8)$$

where $\log N_{2s}(t)/N_{2s}(o)$ can be replaced by $\log S_s(t)/S_s(o)$, if the peak areas are proportional to the number of moles, i.e., in the linearity range of the detector.

K_s^{∞} is then:

$$K_s^{\infty} = - A \frac{N_{2S}^L}{1 - x_g} \, \frac{1}{\dfrac{1}{1 - y_S} \dfrac{D'_{2g} P_o}{Z_{go} R T_r} + A \dfrac{PV}{ZRT}} \qquad (9)$$

with:

$$A = \frac{\log \dfrac{S_s(t)}{S_s(o)}}{t} \qquad (10)$$

ERROR ESTIMATION

From Eq. 9

$$\frac{\delta K_s^{\infty}}{K_s^{\infty}} = \frac{|\delta A|}{A} + \frac{|\delta N_{2S}^L|}{N_{2S}^L} + \frac{|\delta x_g|}{1 - x_g} + \frac{|\delta (B + C)|}{B + C} \qquad (11)$$

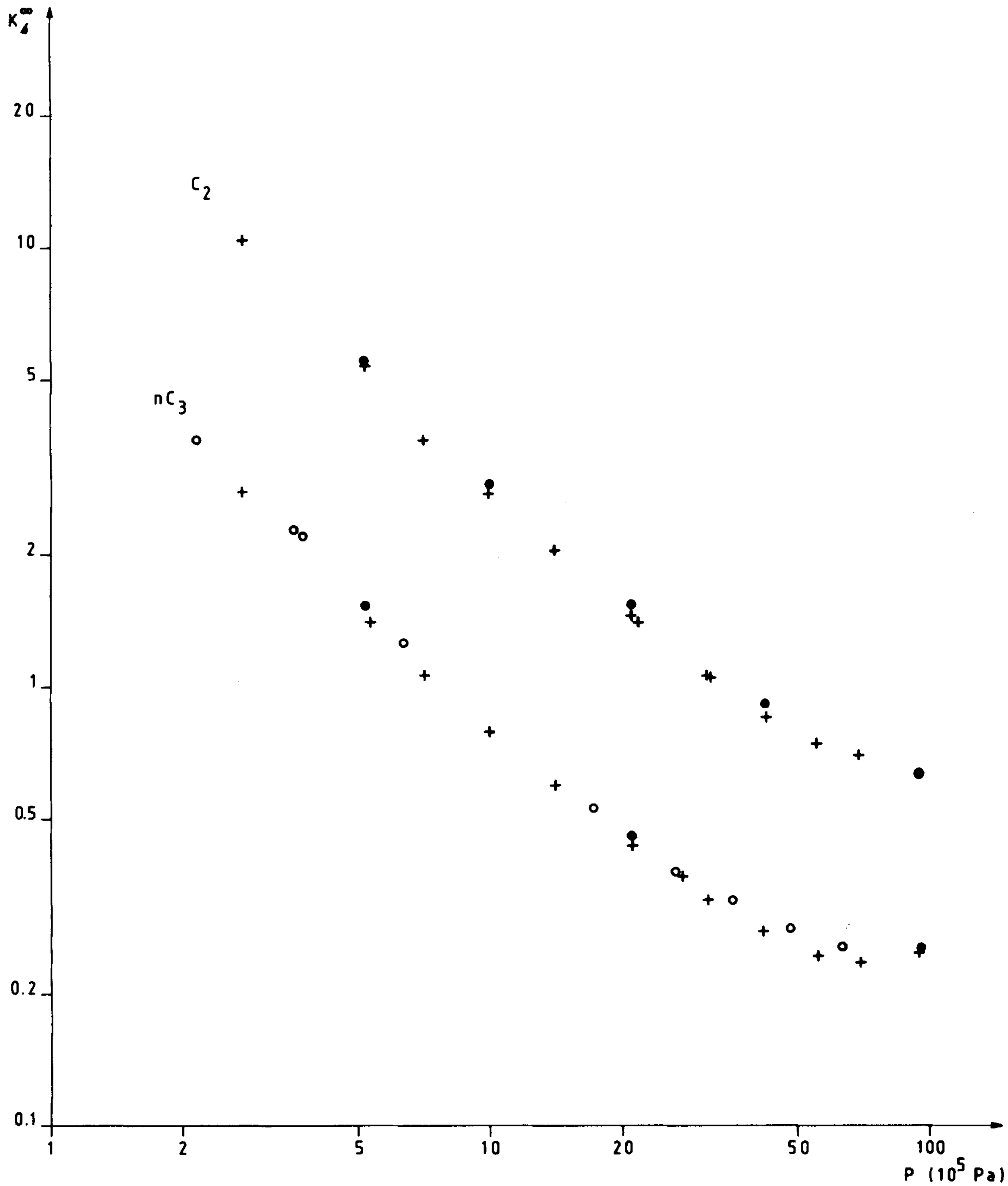

Figure 4. *K* values for ethane and propane at infinite dilution in the methane-n-decane system: *T* = 294.25 K. ● = our results; + = Stalkup and Kobayashi (1963b); ○ = Koonce and Kobayashi (1964).

where

$$B = \frac{1}{1 - y_S}\frac{D'_{2g}P_o}{Z_{go}RT_r}$$

and

$$C = A\frac{PV}{ZRT}; \quad V = V_T - \frac{N^L_{2S}}{1 - x_g}v^{SL}$$

$\delta A/A$ is close to 1%, $\delta P/P \leqslant 1\%$, $\delta T/T \leqslant 0.4\%$, $\delta N^L_{2S}/N^L_{2S}$ is negligible. $\delta x_g/(1 - x_g)$ and $\delta v^{SL}/v^{SL}$ are estimated from literature data to 1%. (See Tables 2 to 5 for K_s^∞ calculated with two data sources.) $\delta D'_{2g}/D'_{2g} \leqslant 1\%$. ($D'_{2g}$ is measured through a bubble flowmeter.) $\delta P_o/P_o \leqslant 0.1\%$, y_S is very often negligible compared to 1. At 294.25, we set $y_S = 0$ and at 344.25 K we used data of Reamer et al. (1942, 1949). For these two cases $\delta y_S/(1 - y_S) < 0.1\%$, Z_{go} is calculated within 0.1% by using a three-parameter correlation (Lee and Kessler, 1975). Z is obtained assuming that the vapor phase in the dilutor is pure methane ($y_S < 7\ 10^{-3}$ at 344.25 K) from tables of Goodwin (1974). Accuracy on Z is then better than 1.5%. $\delta V_T/V_T < 0.5\%$. $\delta C/C$ is then always less than 15%. C is a corrective term for the amount of solute in vapor phase in the dilutor which is small compared to B (of the order of 5% of B in the case of a light solute (Table 2) and 1% for a heavier one, Table 5).

In these conditions $\delta(B + C)/(B + C)$ is less than 2.5%.

Finally this calculation gives a maximum error for K_s^∞ of 4.5% which is an overestimation of the experimental error in this type of measurement. It is estimated by the authors at less than 2%.

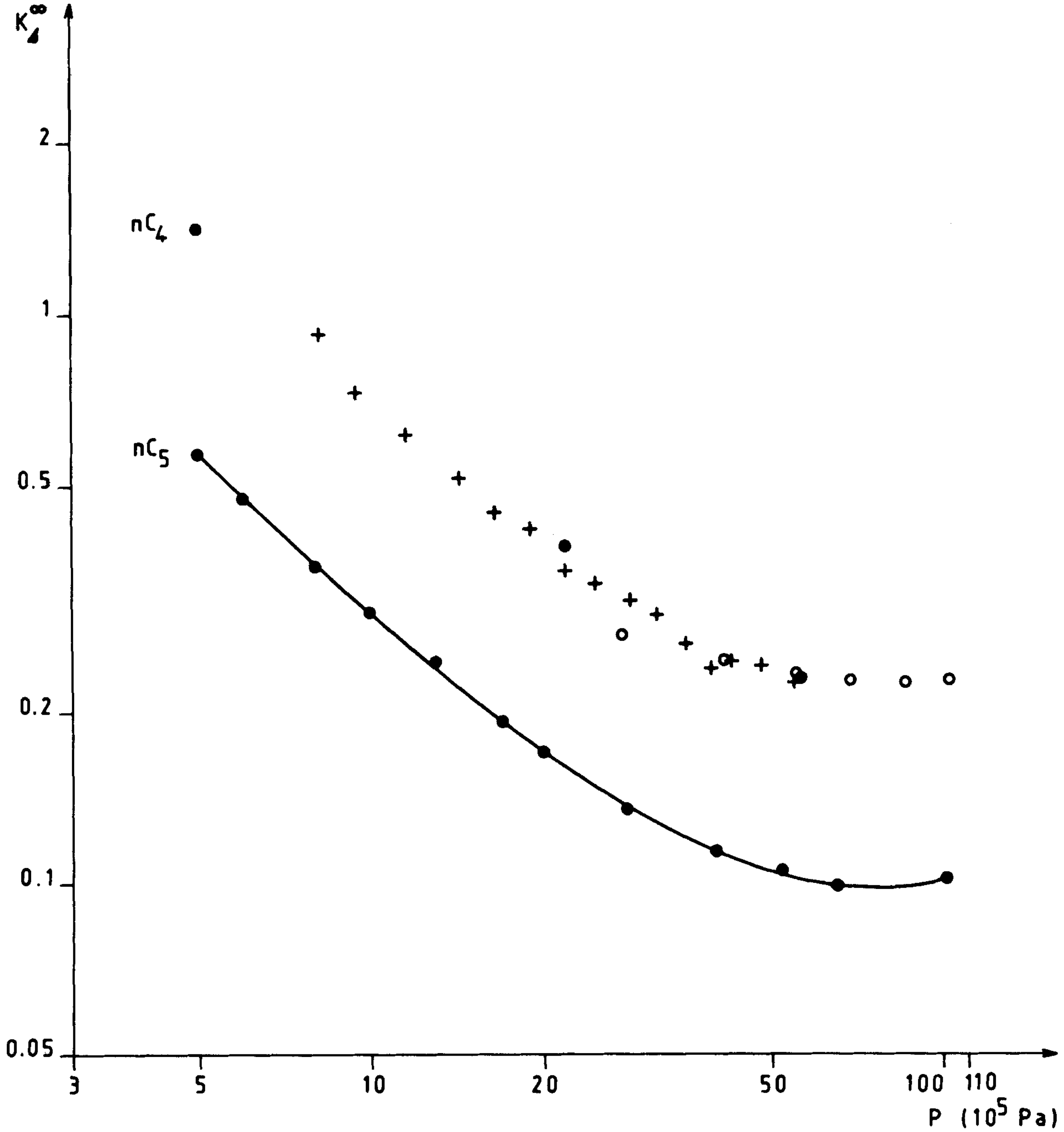

Figure 5. *K* values for n-butane and n-pentane at infinite dilution in the methane-n-decane system: T = 344.25 K. ● = our results; + = Stalkup and Kobayashi (1963b); ○ = Reamer et al. (1949).

TABLE 5. *K* VALUES FOR N-PENTANE AT INFINITE DILUTION IN THE METHANE-N-DECANE SYSTEM: T = 344.25 K

Pres., 10^5 Pa	$\frac{C}{B}$,* %	$K_s^{\infty a}$	$\frac{C}{B}$,** %	$K_s^{\infty b}$
5.0			0.4	0.568
6.0			0.5	0.473
8.0			0.5	0.360
10.0	0.58_5	0.300	0.58	0.301
13.0	0.58	0.244	0.57_5	0.245
17.0_5	0.55	0.193	0.54	0.194
20.1	0.55	0.169	0.54	0.170
28.1	0.58	0.134	0.57	0.135
40.1	0.66	0.113	0.65	0.114
52.1	0.75	0.104	0.73	0.105
65.1_5	0.9	0.098	0.89	0.099
101.2	1.1	0.100	1.0	0.103

For *, ** and [a], see Table 2; for [b], see Table 4.

RESULTS AND DISCUSSION

Origin and purity of all chemicals used are reported in Table 1. They were used without any further purification.

In order to test this new method, partition coefficients of ethane, propane, n-butane at infinite dilution in the system methane-n-decane have been determined at 294.25°C (ethane, propane) and 344.25 K (n-butane) up to 95.35 10^5 Pa (Tables 2 to 4). Comparisons with literature data are illustrated in Figures 4 and 5. K_s^∞ values plotted in these figures are either values derived from the unique set of vapor-liquid data available or the average of two values calculated from two data sources.

Reproducibility of our results is very good (within 1% in the worst cases). Correction for vapor space does not introduce a systematic deviation on K_s^∞ values and our data are not scattered (Figure 5). Our data are not in good agreement with those of Stalkup and Kobayashi (1963b), maximum deviation reaches 10% at low pressures and decreases at high pressures. The technique used by Stalkup and Kobayashi is based on gas chromatography by measuring retention times. The incertitudes indicated by these authors is between 3 and 5% for n-butane are between 10 and 15% for ethane. Koonce and Kobayashi (1964) used a similar technique, but several improvements were made in the data treatment especially in determination of the "free" gas retention volume, the compressibility factor of the elution gas and total number of moles of fixed liquid on the column packing. They did show that the poor determination, by Stalkup, of these parameters, mainly "free" gas volume, led to too low K_s^∞ values; this is confirmed by our results. Koonce and Kobayashi report accuracy of their results of 1.5%. The agreement with present data is good (Figure 4). For butane, data of Reamer et al. (1949) are represented in Figure 5 at 344.25 K; they were obtained with a static method. The disagreement with our data increases when pressures become lower.

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NOTATION

D = total molar gas flow rate at the inlet of the saturator cell (mol·s^{-1})
D_1 = total molar gas flow rate between the saturator and the dilutor (mol·s^{-1})
D_2 = total molar gas flow rate out of the dilutor cell (mol·s^{-1})
K = partition coefficient
N_1 = number of moles in the saturator (mol)
N_2 = number of moles in the dilutor (mol)
P = pressure in the dilutor
P_{at} = atmospheric pressure
P_o = atmospheric pressure corrected for water vapor pressure at T_r room temperature (Pa)
R = gas constant (cm^3·Pa·g·mol^{-1}·K^{-1})
S = area of chromatographic peaks (arbitrary units)
T = temperature of the equilibrium (K)
T_r = room temperature (K)
t = time (s)
V = volume of vapor space in the dilutor cell (cm^3)
v = molar volume (cm^3·mol^{-1})
x_i = liquid mole fraction of component i in the dilutor
y_i = vapor mole fraction of component i in the dilutor
Z = compressibility factor of vapor phase in the dilutor cell
Z_{go} = compressibility factor of the pure carrier gas at atmospheric pressure and room temperature
= very close to

Subscripts

1,2 = saturator and dilutor for parameters of flow coming out of them
g = carrier gas
s = solute
S = solvent

Superscripts

L = liquid
S = saturated property
V = vapor
∞ = infinite dilution
$'$ = volumetric property
$-$ = mean value

APPENDIX

Mass balance around the dilutor:
For each component of the mixture, we may write:

$$D_{2g} = D_{1g} - \left(\frac{dN_{2g}}{dt}\right)$$

$$D_{2S} = D_{1S} - \left(\frac{dN_{2S}}{dt}\right)$$

$$D_{2s} = 0 - \left(\frac{dN_{2s}}{dt}\right)$$

Then the total flow rate is:

$$D_2 = D_{1g} + D_{1S} - \left(\frac{dN_{2g}}{dt}\right) - \left(\frac{dN_{2S}}{dt}\right) - \left(\frac{dN_{2s}}{dt}\right)$$

in proper condition of operation with a solute at infinite dilution, we have

$$\left(\frac{dN_{2S}}{dt}\right) \# 0 \text{ and } \left(\frac{dN_{2g}}{dt}\right) \# 0$$

then

$$D_2 = D_{1g} + D_{1S} - \left(\frac{dN_{2s}}{dt}\right)$$

or

$$D_2 = D_{2g} + D_{2S} - \left(\frac{dN_{2s}}{dt}\right)$$

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Selective Electrorefining with Liquid Membranes

Liquid membranes containing macrocyclic polyethers can be used to electrorefine metals. This purification depends on the selective reaction of the polyether and the metal cation to produce a charged product. The amount of this product is found to be proportional to the square root of the amount of polyester present. Results for silver and copper purification illustrate the ideas involved.

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Electrorefining is a method of purifying metals using an electrolytic cell. An impure metal anode is dissolved, and purer metal is redeposited at the cathode. If the impurities are insoluable in the electrolyte, they fall to the bottom of the cell, and can be separated and further refined. Electrorefining is often used to remove insoluable noble metals from copper. However, it can not be used if the impurities also dissolve in the electrolyte and then reprecipitate at the cathode (Yannopoulous and Argawol, 1976).

This work explores the feasibility of using a liquid membrane to make electrorefining more selective. Such membranes are an organic solution of a mobile carrier, a water-insoluble solute which reacts selectively with a particular metal ion and facilitates its transport (Cussler and Evans, 1980). These membranes are analogs to those found in living systems (Eisenmen, 1975). They are frequently suggested as a route to commercially attractive separations, especially for heavy metals (Schwind et al., 1978; Cahn et al., 1980).

In this paper, we investigate two different membrane geometries suitable for selective electrorefining. First, we place a liquid membrane like those used for selective separations between the anode and the cathode of an electrocyclic cell. This geometry requires supporting this ultra thin, liquid membrane. Second, we coat the cathode itself with the liquid membrane. This method provides automatic membrane support but can be compromised by reaction of membrane components at the cathode.

CONCLUSIONS AND SIGNIFICANCE

We have developed liquid membranes which can selectively electrorefine silver and copper. The selectivity depends on the formation and diffusion of charged complexes of ions and a macrocyclic polyether, 18-crown-6 or benzo-15 crown-5. The key feature of these complexes is their ionic charge necessary for the electrorefining. Previously reported complexes used in other types of membrane separations were usually ion pairs with no net charge (Hochhauser and Cussler, 1975; Christensen et al., 1980). Obtaining ionic complexes requires carefully balancing membrane properties like the solvent dielectric constant, the cation-carrier reaction, and the solubility of available anions.

The results for a liquid membrane mounted in solution between anode and cathode are in agreement with theoretical predictions developed in this paper. These predictions assume that the rate limiting step in the process is the ion transport across the liquid membrane caused by an electrical potential, and so are accurate only for thick membranes and reversible electrodes. We emphasized this case because we wanted to focus on the membrane properties, rather than on the electrode reactions. The results for a liquid membrane coating the cathode show that silver can be transported across this membrane and deposited in pure form. This process is often compromised by electrode reactions of the membrane solvent or the mobile carrier.

Thus we have demonstrated the technical feasibility of selective electrorefining using liquid membranes. Achieving commercial operation will require developing a thin, stable membrane with selectively high electrical conductivity. We do not feel that making the membrane thin and stable will be a major problem: membrane technology for these attributes is well developed. We do feel that developing a membrane which is both selective and conductive is harder, for our experience suggests that high selectivity often means low conductivity, and *vice versa*.

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