

A MODIFICATION OF THE INERT GAS STRIPPING METHOD FOR MEASURING THE LIMITING ACTIVITY COEFFICIENT

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Received July 31, 1989

Accepted October 9, 1989

A modification of the inert gas stripping method for measuring the limiting activity coefficient is proposed. Compared to the procedure used so far, the modification consists of a change in the apparatus arrangement and measurement of the decrease in solute concentration in the liquid phase only. The method has been tested by measuring the limiting activity coefficients of heptane in N-methylpyrrolidone at 25, 50 and 55°C. The results are in good agreement with published values determined by various methods.

One of the most frequently used experimental methods for direct measurement of the limiting activity coefficient is that of inert gas stripping proposed by Leroi and co-workers¹. The basis of the method is a measurement of the desorption of a solute from a solution as a function of time. The solute is present in the solution in a very low concentration and is desorbed by the passage of an inert gas at a constant flow rate. During the desorption, samples of the vapour phase are withdrawn and their compositions are determined. It is important to ensure a large gas-liquid mixture interface, a sufficiently long time of contact between the two phases, and good dispersion of bubbles in the liquid. Under such conditions, the gas leaving the saturation vessel may be expected to be very close to equilibrium with the liquid mixture. In the original apparatus of Leroi and co-workers¹, the stripping inert gas is fed to the liquid phase through a tube terminated with a frit. In order to prevent the vapour or organic substances to condense in the gas stream leaving the saturation vessel, both the outlet and the sampling valve are heated. Similar arrangements have also been used by other investigators²⁻⁴. Richon and co-workers⁵ have modified the original saturation vessel so that the stripping inert gas is fed through suitably positioned capillaries to the bottom of the vessel and the gas exits through a concentric annulus at the top. The positioning and shape of the outlet should help ensure gas-phase homogeneity, and hence reproducibility of the results. The gas-phase homogeneity and the absence of vapour condensation in the stream of the stripping or carrier inert gas before entry to the chromatographic column are important features which require special attention.

Our modification of the method involves the measurement of the decrease in solute concentration in the liquid phase which, according to a basic assumption, is in equilibrium with the gas leaving the vessel. In this case, all that is needed is to ensure homogeneity of the liquid phase and perfect saturation of the gas with the vapour. No other modifications or control of the gas-phase condition are necessary. We have, however, to modify the relationships for calculating the limiting activity coefficients from the experimental results.

THEORETICAL

Leroi and co-workers¹ have derived equations allowing the limiting activity coefficient, $\gamma_{\text{sol}}^{\infty}$, of a solute to be calculated from measured variation in the solute concentration in an inert gas stream leaving the saturation vessel. They started from the assumption of an equilibrium between the solute, the solvent and the inert gas:

$$x_{\text{sol}}\gamma_{\text{sol}}f_{\text{sol}}^{\text{OL}}I_{\text{sol}} = y_{\text{sol}}\phi_{\text{sol}}p \quad (1)$$

$$x_s\gamma_s f_s^{\text{OL}}I_s = y_s\phi_s p \quad (2)$$

$$x_{\text{CG}}H_{\text{CG}} = y_{\text{CG}}\phi_{\text{CG}}p \quad (3)$$

For very dilute solutions ($x_{\text{sol}} < 10^{-3}$), the activity coefficient may be approximated by its limiting value. Further assumptions, namely that the mole fraction x_s of the solvent in solution and its activity coefficient γ_s are equal to unity, the vapour phase shows an ideal behaviour, and the carrier gas solubility is negligible, together with the overall material-balance equation for the saturation vessel

$$\dot{V}_G = \dot{V}_I - \frac{RT}{p} \left(\frac{dn}{d\tau} + \frac{dN}{d\tau} \right) \quad (4)$$

and relationships for the loss of the solute ($-dn$) or solvent ($-dN$) in time $d\tau$

$$dn = -y_{\text{sol}}p(\dot{V}_G/RT) d\tau \quad (5)$$

$$dN = -y_s p(\dot{V}_G/RT) d\tau \quad (6)$$

were used to derive basic differential equations whose integration and rearrangement provided a relationship for the limiting activity coefficient $\gamma_{\text{sol}}^{\infty}$.

For our procedure, which starts from changes in the solute concentration in the liquid phase, we adapt Eqs (1) to (6) so that the final relationship contains a term expressing the change in the mole fraction of solute in the liquid phase as a function of time.

Starting from the same assumptions as used by Leroi and co-workers¹ for the losses of solute ($-dn$) and solvent ($-dN$) in time $d\tau$ as a result of desorption by the inert gas, we obtain:

$$\frac{dn}{d\tau} = -x_{\text{sol}}\gamma_{\text{sol}}^{\infty}p_{\text{sol}}^0I_{\text{sol}}\frac{\dot{V}_1}{RT}\left[\frac{p}{p - x_{\text{sol}}\gamma_{\text{sol}}^{\infty}p_{\text{sol}}^0I_{\text{sol}} - p_s^0I_s}\right] \quad (7)$$

$$\frac{dN}{d\tau} = -p_s^0I_s\frac{\dot{V}_1}{RT}\left[\frac{p}{p - x_{\text{sol}}\gamma_{\text{sol}}^{\infty}p_{\text{sol}}^0I_{\text{sol}} - p_s^0I_s}\right]. \quad (8)$$

Using the notation

$$p_{\text{sol}}^0I_{\text{sol}} = C_1 \quad (9)$$

$$p_s^0I_s = C_2 \quad (10)$$

$$\dot{V}_1/RT = C_3 \quad (11)$$

and assuming that

$$x_{\text{sol}} \approx n/N \quad (12)$$

$$n = Nx_{\text{sol}} \quad (13)$$

$$dn = N dx_{\text{sol}} + x_{\text{sol}} dN \quad (14)$$

we obtain from Eq. (7) the following relationship for the limiting activity coefficient of solute:

$$\gamma_{\text{sol}}^{\infty} = -\frac{N}{C_1C_3}\left(\frac{d\ln x_{\text{sol}}}{d\tau}\right)\left(\frac{p - x_{\text{sol}}\gamma_{\text{sol}}^{\infty}C_1 - C_2}{p}\right) + \frac{C_2}{C_1}. \quad (15)$$

The amount N of solvent at time τ can be expressed from Eq. (8) as

$$N = N_0 - \int_{\tau_0}^{\tau} C_2C_3\left(\frac{p}{p - x_{\text{sol}}\gamma_{\text{sol}}^{\infty}C_1 - C_2}\right)d\tau. \quad (16)$$

The integral in Eq. (16) may be evaluated in various ways:

a) if we replace the mole fraction x_{sol} of solute by its mean value $\bar{x} = (x_0 + x)/2$, where x_0 and x are the mole fractions of solute at times τ_0 and τ , respectively, then

$$N = N_0 - C_2C_3\frac{p}{p - \bar{x}\gamma_{\text{sol}}^{\infty}C_1 - C_2}(\tau - \tau_0); \quad (17)$$

b) assuming that

$$p \approx p - \bar{x}\gamma_{\text{sol}}^{\infty}C_1 - C_2 \quad (18)$$

we obtain

$$N = N_0 - C_2C_3(\tau - \tau_0); \quad (19)$$

c) numerical integration without any simplifying assumptions.

Since Eqs (15) and (16) involve implicitly the limiting activity coefficient $\gamma_{\text{sol}}^{\infty}$, they must be solved by iteration, using as the initial estimate a value of $\gamma_{\text{sol}}^{\infty}$ calculated from the simplified relationship

$$\gamma_{\text{sol}}^{\infty} = -N_0 \left(\frac{d \ln x_{\text{sol}}}{d\tau} \right) \frac{RT}{p_{\text{sol}}^0 \dot{V}_1} \quad (20)$$

EXPERIMENTAL

Apparatus

A scheme of the apparatus for measuring limiting activity coefficients by inert gas stripping method is given in Fig. 1. An inert gas (N_2) is introduced from pressure vessel 1 through magnetic valve 3 controlled by manostat 4 into levelling vessel 5 of about 2 dm³ volume. After drying by 3A molecular sieves 6, nitrogen from the levelling vessel flows through valve 2 and capillary restrictor 9 into saturation vessel 10. The capillary is placed in constant-temperature jacket 11 and is sized so that the nitrogen flow rate at an overpressure between 7 and 20 kPa (measured by U-manometer 7 with an accuracy of 50 Pa) ranges from 0.04 to 0.12 cm³/s. Before measurement, the calibration of the volumetric flow rate of nitrogen vs its overpressure relative to atmospheric pressure was determined experimentally. The obtained dependence $\dot{V}_1 = f(p(N_2))$ was quadratic and

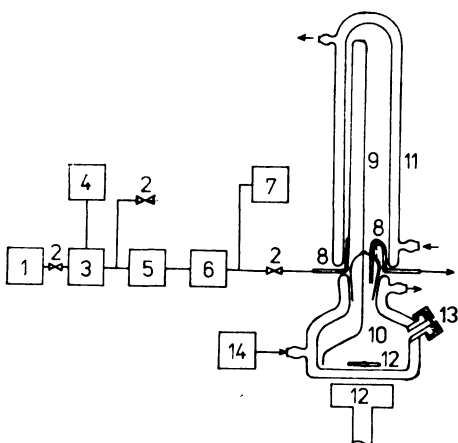


FIG. 1
Schematic drawing of the apparatus for measuring the limiting activity coefficient: 1 pressure vessel, 2 valve, 3 magnetic valve, 4 manostat, 5 levelling vessel, 6 vessel with molecular sieves, 7 U-manometer, 8 metal tube, 9 metal capillary, 10 saturation vessel, 11 jacket for thermostating the capillary, 12 magnetic stirrer, 13 sampling aperture, 14 thermostat

the standard deviation of calculated volumetric flow rates ranged from 3.4 to 6.3 · 10⁻⁴ cm³/s. The capillary restrictor is terminated close to the vessel wall, 1–2 mm from the bottom. Magnetic stirrer 12 provides for intense rotation of the liquid. Simultaneous rotation of gas bubbles increases the time of contact between the two phases. Moreover, the rotating liquid keeps the gas above the surface in angular motion, so extending further the contact time. In this way, the gas-liquid contact time is increased several times compared with bubble passage without agitation. The gas exits from the saturation vessel into the atmosphere through metal tube 8 with negligible hydrodynamic resistance, so that there is practically the atmospheric pressure in the vessel. Samples are taken with a microsyringe through seal 13 with a rubber septum.

Procedure

Before measurement, the dependence of the mass fraction of heptane in solution on the surface fraction obtained from chromatographic analysis is determined. For the test system, the calibration is linear.

Prior to measurement, the whole apparatus is flushed with the inert gas. An amount of solvent with a volume of 10 to 11 cm³ is weighed into the saturation vessel. After turning on the magnetic stirrer, the vessel (10) and the jacket (11) with the capillary restrictor are thermostatted at the working temperature. Then the inert gas is admitted and the required amount of solute ($x_{s,01} \approx 10^{-3}$) is injected with a microsyringe. At time intervals whose length depends on the rate of solute stripping from the solution (about 30 min for the given system), liquid samples are withdrawn for chromatographic analysis.

Measurement of the Degree of Gas Saturation

A prerequisite for the success of the work is that the carrier gas must be saturated with the vapour of the component being stripped. This was verified by measuring the benzene content of the carrier gas after bubbling it through benzene at a temperature of 20°C. Nitrogen saturated with benzene was led from the saturation vessel through a U-tube filled with active carbon. The mass gain of the active carbon after the bubbling was used to calculate the partial pressure of benzene in the carrier gas and this value was compared with the saturated vapour pressure at the temperature of the saturation vessel.

Chemicals

The apparatus was tested by measuring the limiting activity coefficient of heptane in N-methylpyrrolidone (NMP). The measurement was made using n-heptane for UV spectroscopy (Lachema, Brno) and NMP prepared from a technical product used in the concern of Slovnaft by double vacuum fractional distillation on a column with an efficiency of about 10 TP and subsequent drying by 3A molecular sieves. The purity of the chemicals as determined by chromatography was better than 99.8%.

RESULTS

The results for the degree of saturation of the gas at the outlet of the saturation vessel with benzene at 20°C are given in Table I. As seen from the table, the gas leaving the vessel at the given flow rates is 100% saturated with benzene, within the limits of experimental error.

In addition to the directly measured quantities (p , T , \dot{V}_1 , N_0 , τ), some other have to be calculated before the limiting activity coefficient can be computed from the set of equations (15) and (16).

a) The slope of the $\ln x_{\text{sol}} = f(\tau)$ line is obtained by the least squares method from experimental $[\tau, x_{\text{sol}}]$ points.

b) As indicated in the theoretical part, the amount N of solvent at time τ can be calculated in several ways. It has been found that all the three procedures outlined above give the same result for our system, indicating that assumption (18) holds true for the system investigated.

TABLE I
The degree of saturation, β , of the gas leaving the saturation vessel with benzene

$\dot{V}_1 \cdot 10^6, \text{m}^3/\text{s}$	0.074	0.107	0.112
β	1.00	0.99	1.01

TABLE II
Comparison of limiting activity coefficients of heptane in NMP measured by various methods. DIL inert gas stripping method; GLC retention time method; EX extrapolation of equilibrium data or of activity coefficients measured at finite concentrations; STAT calculated from data measured on a static apparatus; values measured by us are printed in italics

$t, ^\circ\text{C}$	γ^∞	Method
25	<i>16.3</i>	—
	15.1 ⁶	GLC
	19.1 ⁷	GLC
	16.24 ²	DIL
	16.2 ²	EX
	16.27 ²	EX
50	<i>12.7</i>	—
	12.3 ⁶	GLC
	12.6 ⁹	STAT
55	<i>11.4</i>	—
	12.6 ⁷	GLC
	13.1 ⁸	GLC

c) The molar volume of pure NMP for calculating the Poynting correction $I = \exp(\gamma_i^{\text{OL}} p/RT)$ were obtained from critical or reduced quantities by means of the law of corresponding states¹³. The calculated values were $\gamma_{\text{NMP}}^{\text{OL}} = 101.7 \cdot 10^{-6} \text{ m}^3/\text{mol}$. For heptane, a value reported in the literature¹², $\gamma_{\text{hep}}^{\text{OL}} = 152.2 \cdot 10^{-6} \text{ m}^3/\text{mol}$, was used in calculating the limiting activity coefficient.

d) The saturated vapour pressure of heptane was calculated from Antoine's equation using the coefficients published by Dykyj and co-workers¹⁰. The saturated vapour pressures of NMP at 25 and 55°C were calculated in the same way, and the value for 50°C was obtained by extrapolation of experimental data published by Aim¹¹ ($p_{\text{NMP}}^0 = 224.5 \text{ Pa}$).

The system NMP–heptane was chosen for assessing the adequacy of the proposed method because experimental data for the limiting activity coefficient of heptane in NMP obtained by several methods were available in the literature^{1,6–9}. The value of γ^∞ obtained by the retention time method is usually higher^{7,8} than that measured by the inert gas stripping method (Leroi and co-workers¹, γ^∞ measured by us). This discrepancy has been ascribed^{1,4} to surface phenomena occurring during the measurement on a chromatographic column.

As seen from Table II, the values measured by the inert gas stripping method are in very good agreement with each other, as well as with the value calculated from data measured on a static apparatus⁹ and that obtained by extrapolation¹. The difference between repeated measurements of the limiting activity coefficient of heptane in NMP is not larger than 1–2%. It may therefore be concluded that the proposed modification of the inert gas stripping method involving the analysis of the liquid phase is suitable for measuring the activity coefficients in infinitely dilute solutions.

LIST OF SYMBOLS

C_1, C_2, C_3	coefficients defined by Eqs (9), (10) and (11)
$I =$	$\exp(\gamma_i^{\text{OL}} p/RT)$, Poynting's correction
f	fugacity
H	Henry's coefficient
n	amount of solute
N	amount of solvent
p	pressure
R	gas constant
t	temperature
T	absolute temperature
\dot{V}	volumetric flow rate
γ	molar volume
x	mole fraction in the liquid phase
y	mole fraction in the vapour phase
β	degree of saturation

γ	activity coefficient
ϕ	fugacity coefficient
τ	time

Subscripts

CG	carrier gas
G	gas at the outlet of saturation vessel
i	component
I	inert gas
0	quantity at time $\tau = 0$
s	solvent
sol	solute

Superscripts

∞	infinitely dilute solution
0	pure component
—	mean value
L	liquid component

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Translated by M. Škubalová.