

A DIFFERENTIAL STATIC APPARATUS FOR THE INVESTIGATION OF THE  
INFINITELY DILUTED REGION

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ABSTRACT

This work proposes a method for the determination of data at infinite dilution and at very low concentration based on the isothermal measurement of the difference in pressure between two static cells containing the pure component and the mixture respectively. The method is particularly suitable for investigating binary systems whose components differ strongly in volatility, and when other methods such as gas liquid chromatography or ebulliometry fail.

INTRODUCTION

There is a demand for accurate experimental methods in order to have reliable vapor-liquid equilibrium data (VLE) essential in the development of separation processes. In addition thermodynamic models for fluid phase equilibria generally include adjustable parameters which must be determined from experimental data. These parameters are directly related to the activity coefficients at infinite dilution of the binary mixtures.

It has already been stressed how important is the investigation of the dilute region both theoretically and practically. Data in this concentration range should always be measured by "ad hoc" experimental methods and not obtained by dangerous extrapolation.

For the determination of data at infinite dilution we propose a method based on the isothermal measurement of the difference in pressure between two static cells, one containing the pure solvent and the other the solute infinitely diluted in the solvent.

This apparatus is particularly suitable for investigating binary systems whose components differ strongly in volatility, thus filling a gap in the experimental methods available for the determination of the activity coefficients of non volatile compounds infinitely diluted in volatile solvents.

The apparatus and the procedure were checked on pure component vapour pressure of ethanol and n. heptane and on the binary system n. hexadecane - ethanol.

## THEORY

Gautreaux and Coates (1955) derived four expressions for the activity coefficients at infinite dilution in terms of pure component properties and the limiting slopes of pressure and temperature with respect to liquid and vapour phase composition.

The determination of the limiting slope of the temperature vs. liquid composition at constant pressure (measurement of boiling point elevation) leads to the differential ebulliometric technique (Eckert et al. 1981, Loblen and Prausnitz 1982, Dohnal and Novotna 1985). This method is, in principle, rather simple and rapid because it implies a gravimetric determination of composition and the use of a dynamic still which assures rapidity of measurements. On the other hand the method requires a very careful calibration (Rogalsky et al. 1977), does not hold for high boiling substances (Dohnal and Novotna 1985) and in the case of high relative volatility of the two compounds the correction factor becomes very significant (Alessi et al. 1985).

These arguments led us to propose a new method based on the determination of the limiting slope of the pressure vs. liquid composition at constant temperature. The method is particularly convenient for the following reasons: a) the composition is determined volumetrically rather than by analysis of samples; b) the static stills assure a very precise pressure measurement; c) temperature stability is easily established with an appropriate liquid bath. The method can be simplified by using a piston injector to vary the composition inside the cells, as suggested by Gibbs and Van Ness (1972).

The equation derived by Gautreaux and Coates (1955) for a binary system at isothermal conditions is:

$$\gamma_1^\infty = (P_2^0 \varphi_1^0) / (P_1^0 \varphi_1^0) \left( 1/P_2^0 \left( \partial P / \partial x_1 \right)_\infty + \varphi_2^0 / \varphi_2^0 - \partial(\varphi_2^0 / \varphi_2^0) / \partial x_1 \right) \quad (1)$$

or in the case of vapour phase ideality:

$$\gamma_1^\infty = P_2^0 / P_1^0 \left( 1 + 1/P_2^0 \left( \partial P / \partial x_1 \right)_\infty \right) \quad (2)$$

Equation (1) makes no assumptions about liquid phase non-ideality except for the finiteness of the infinite dilution activity coefficient and its derivatives with respect to composition. The fugacity coefficients can be estimated at low pressure by a correlation for the second virial coefficient such as that proposed by Hyden and O'Connell (1975) or, at high pressure by means of an equation of state. The limiting composition derivative of the pressure is obtained from experimental data.

Equation 1 has the advantage that no functional dependence of the activity coefficients on composition is assumed: extrapolation of pressure differences versus concentration is performed.

Equation (1) (or equation (2) if we disregard vapour phase non

ideality) can be used to examine the sensitivity of infinite dilution activity coefficients to errors in the measured variables using the hypothesis of independent measured variables; the application of the error propagation law to equation (2) leads to an expression for  $d\gamma^\infty$  as a function of the uncertainties in the measured variables (namely the temperature and the limiting slope  $P$  vs.  $x$ .)

$$d\gamma_i^\infty = \left( \frac{\partial P_1^0}{\partial T} P_1^0 - \frac{\partial P_2^0}{\partial T} P_2^0 \right) / P_1^0 P_2^0 \left[ 1 + \left( \frac{\partial P}{\partial x_1} \right) / P_2^0 \right] - \left( \frac{\partial P}{\partial x_1} \frac{\partial P_2^0}{\partial T} \right) / P_1^0 P_2^0 + \left( \frac{\partial^2 P}{\partial x_1 \partial T} \right) / P_1^0 \right] dT - d \left( \frac{\partial P}{\partial x_1} \right) / P_1^0 \quad (3)$$

Equation (3) shows that temperature stability is essential for a correct determination of infinite dilution activity coefficients because it influences all the terms in equation (3).

Small errors in the activity coefficients are also achieved if a correct measure of the limiting slope is performed: in other words concentration and pressure must be carefully measured.

This slope is calculated by fitting  $\Delta P$  (difference in pressure between the reference cell containing pure component 2 and the cell containing pure component 2 plus a very small amount of component 1) vs.  $x$  data by means of a mathematically flexible model using a computer program based on the principle of maximum likelihood. In this way differences in pressure rather than absolute values are determined, allowing a much higher precision in the measurement. Compositions are determined volumetrically and correction for the vapour phase space is included.

The goodness of the activity coefficients data depends also upon the goodness of the vapour pressure data: in fact eq. 2 shows that the value becomes questionable as the vapour pressure of the solute goes to zero. In this case we suggest to report the value  $\gamma^\infty P^0$  rather than the infinite dilution activity coefficient also because this quantity is directly used in phase equilibria calculation.

#### EXPERIMENTAL SECTION

Many researchers (Tomlins and Marsh (1976), Aim (1978), Maher and Smith (1979), Legret et al. (1980), Mentzer et al. (1982), Kolbe and Gmehling (1980)) have attempted to measure VLE by using a static apparatus since Gibbs and Van Ness in 1972 suggested a rapid and accurate method based on piston-injector devices for introducing the components of the mixture in the equilibrium cell.

In this paper we are concerned with the extension of the method for the determination of activity coefficients at infinite dilution especially for those binary systems which are difficult to study by other methods.

A schematic diagram of the experimental system is shown in figure 1 in which the major components of the static apparatus are evidenced. The apparatus herein described consists of two cells and operates according to the principle proposed by Gibbs and Van Ness (1972).

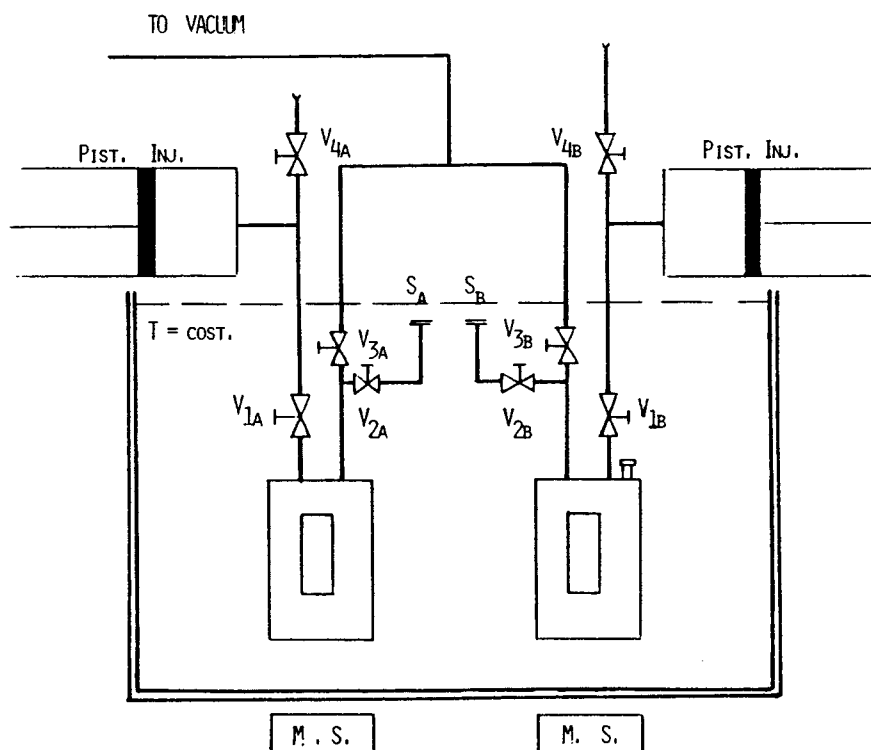


Figure 1: the experimental apparatus.

The main difference is that the component which is present in small concentration (solute) is injected into one the cell A, containing a known amount of the solvent, by means of a gas-tight syringe. The second cell (B) contains only the solvent and therefore can be considered as the reference cell. Differences in pressure at constant temperature are then determined for additions of known amount of the solute in the cell A. The total pressures above the liquids in the cells A and B are measured by pressure gages. The two cells are identical; they are constructed in AISI 316 stainless steel and they have a total volume of 53 cm<sup>3</sup> (including the stainless steel pipes connecting the cells to the pressure gages). The mixing of the liquid is achieved by means of a teflon coated iron bar and a magnetic drive powered by an electric motor with variable speed. Valves are bellows valves (Nupro model SS4H-THS). Helium tested glass to stainless steel seals (Cajon G304-4-GH-3) are employed to insure tightness of the connections. The leak rate of the total system (cells plus connections to gage and to pump) never exceeded .001 Pacm<sup>3</sup>/s.

For maintaining constant the temperature of the cells, a two stage water bath was constructed. The bath had a vertical 45 cm travel and could be easily raised to submerge the cells and lowered to make them accessible. The internal bath had no heating of its

own and was stirred by a heat insulated propeller. The external thermostat was an F3 Haake unit with a circulation pump and a temperature controller. In the temperature range 273 - 333 K, the temperature stability for 6 hours was  $\pm 0.005$  K. The temperature was measured by a quartz thermometer developed in our laboratories with two Pt 100 probes. The probes were situated in the internal thermostat so that their sensors could be in close proximity to the liquid surrounding the cells. Probe calibrations were performed by using a triple point cell (water) and a Leeds and Northrup standard platinum resistance thermometer. The temperatures measured are estimated to be within  $\pm 0.001$  K of the true temperatures.

The equilibrium vapour pressure was measured by pressure gage model APR 015. Calibration of the pressure gages was made by connecting them to a vacuum achieved by means of granulated active carbon, which was evacuated at 673 K, by immersing in liquid nitrogen. The accuracy of the vapour pressure measurements is estimated to be  $\pm 1$  Pa in differential and  $\pm 10$  Pa in absolute mode.

Before the experiments are performed it is important to degas the pure components carefully, as the presence of residual gases dissolved in the solution may lead to large errors in absolute pressure determination. Aim (1978) suggested as criterion for complete degassing the constancy of vapour pressure within the sensitivity limits of the pressure gage after flushing out the vapour phase. The procedure for degassing is essentially that proposed by Hermsen and Prausnitz (1963) and consists of distillation under vacuum at total reflux and a programmed sampling of the top product by means of two solenoid valves (Leybold Heraeus mod 17472). In this respect the method is also similar to that proposed by Van Ness and Abbott (1978) and, at least in principle, to that proposed by Aim. Complete degassing is normally achieved in about 20-25 hours of continuous running.

After degassing, the pure liquid (the solvent) is transferred into the piston-injector device and stored in a compressed state (about .5 MPa). This device (Luwar) consists of a hand operated piston pump, i.e. a piston which is driven via a handwheel and a spindle, which forces the liquid out of a cylinder. The volume displaced is directly proportional to the advance of the piston. For the conversion from volume to mass, the density of the pure substance is needed as a function of temperature and pressure. A U tube vibrating densimeter (A. Paar Graz mod.601) was used for measuring high pressure density and therefore the isothermal compressibility, when this was not available in the literature. The transfer of the degassed liquids depends on whether the component is the solute or the solvent: the solvent is transferred into the cell through the piston-injector while the solute is transferred by means of a gas-tight syringe (Hamilton).

Once the thermostatic bath has reached stability, connecting lines of the system and piston-injector device are evacuated by means of a vacuum pump. The degassed solvent is then introduced into the piston-injector. The valves in the cells are opened and a known amount of the same solvent is transferred into the two cells: 10 to 25 min. are necessary to attain equilibrium in the cells and

this can be checked by the stability of the pressure. When the vapour pressure of the pure component has been determined, a further amount of the same component is introduced in the reference cell to check whether the measured pressure depends on the amount of substance. Then a known amount of the solute is added in cell A and the pressure, after 10-20 min, is recorded. Repeating this operation several times, one gets the difference between the vapor pressure of the mixture and that of the pure solvent as a function of the solute concentration.

#### MATERIALS

Ethanol and n. heptane (Fluka) were used as purchased. Ethanol was found by gas - liquid chromatography to be approximately 99.98% pure. Hexadecane (Janssen), analytical grade was used as purchased (99%).

#### EXPERIMENTAL DATA AND CALIBRATION

The proposed apparatus has been checked by comparison with data reported in the literature. The deviations between vapour pressures measured with the proposed apparatus and literature data for n. heptane (Willingham et al. 1945) and for ethanol (Ambrose and Sprake 1970) in a wide range of temperature (293.15 - 333.15 K) were always less than 1.2%: the root mean square deviation was 0.41%. No variation has been observed in the measured vapour pressure after flushing out some of the vapour phase.

Table 1 summarizes the data obtained in this work and those reported in the literature. It can be seen that the data of ethanol in hexadecane is in perfect agreement with the literature data obtained by different methods; good agreement is also obtained for n. hexadecane in ethanol.

Table 1: N. hexadecane(1) ethanol(2) system: comparison between measured and literature data.

x1	T(K)	$\overset{\infty}{\underset{\infty}{\gamma}}P$ (kPa)	$\gamma^{\infty}$	$\overset{\infty}{\underset{\infty}{\gamma}}P$ (kPa)	$\gamma^{\infty}$	Ref.
		This work		Literature		
1.0	325.25	651.3	19.98	657.8	20.18	French
	317.15				23.60	Alessi
0.0	303.25	.1430	56.97			
	298.15				59.38	French
	308.15				53.25	French
	325.25	.3151	45.01	.3018	43.12	French
	323.20				46.00	Extr.

Table 2: liquid phase compositione and difference in pressure ( $P - P^\circ$ ) for n. hexadecane (1) - ethanol (2) system at 325.25 K: comparison with data of French et al.

x1	$\Delta P$ (Pa)	x1	$\Delta P$ (Pa)
This work		Literature	
.00112	-36.	.0051	-141.
.00222	-72.	.0101	-276.
.00303	-85.	.0201	-486.
.00420	-122.	.0403	-762.
.00529	-149.		
.00988	-216.		

Table 3: liquid phase compositione and difference in pressure for n. hexadecane (1) - ethanol (2) system at 305.25 K; effect of partial degassing.

x1	$\Delta P$ (Pa)	x1	$\Delta P$ (Pa)
degassed		not degassed	
.00464	-53.	.00226	-26.
.00747	-80.	.00452	-53.
.01016	-120.	.00676	-67.
.01290	-147.	.00900	-93.
.01562	-187.	.01122	-133.
.01833	-227.	.01344	-160.
.02102	-280.		

$\gamma^\infty P = 143 \text{ Pa}$ 
 $\gamma^\infty P = 185 \text{ Pa}$

Table 2 reports the variation of the pressure difference at constant temperature (325.25 K) for subsequent injections of small amount of n. hexadecane (50  $\mu\text{l}$ ) in ethanol. The reproducibility has been checked by repeated runs for the same system at the same temperature obtaining differences in pressure within the experimental error of the method. Subsequent injections of greater amounts of solute (100  $\mu\text{l}$ ) starting from the pure solvent lead to results similar to those obtained by subsequent injections of 50  $\mu\text{l}$ : the difference in P are within the experimental error of the method. Table 2 also shows the comparison between the vapour pressure of the mixture measured by the proposed apparatus and the experimental results obtained by French et al (1979): the agreement between French's data and those obtained in this investigation is within the experimental accuracy.

Table 3 shows typical run of the apparatus for determining the activity coefficients at infinite dilution of hexadecane in ethanol

at 303.25 K. As already mentioned above, in this case it is more correct to report the value of the product  $\gamma^{\text{op}}$ , nevertheless the activity coefficient at infinite dilution can be calculated if the vapour pressure of the hexadecane at 303.25 K is known: in this case the value has been estimated extrapolating the vapour pressure at 325.25 K by using heat of vaporization data. Table 3 reports also the result of a run in which the degassing of the solvent was not complete: a substantial error may rise also in differential measurements if the degassing operation is not carefully done.

In conclusion the  $\Delta P$  vs.  $x$  data obtained are consistent and in good agreement with the literature data of French et al and with the activity coefficients at infinite dilution from different sources.

The apparatus proposed is therefore promising for studying the dilute region of binary mixtures when other methods fail and particularly in the case of high boiling compounds infinitely diluted in low boiling compounds. Accurate measurements of vapour pressure of the solute is required in order to get a precise value of the infinite dilution activity coefficient; however this is not a limitation because the product  $\gamma^{\text{op}}$  can be considered as the data measured.

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#### REFERENCES

- Aim K., 1978 Fluid Phase Equilibria 2:119  
 Alessi P., Kikic I., Alessandrini A., Fermeiglia M., 1982, J.Chem. Eng. Data 27:445  
 Alessi P., Fermeiglia M., Kikic I., Paper presented at the 8 Sem. on Applied Thermodynamic, Trieste  
 Ambrose D., Sprake C.H.S., 1970, J.Chem.Thermod. 2:631  
 Dohnal V., Novotna M., 1985, Fluid Phase Equilibria, 23:303  
 Eckert C.A., Newman B.A., Nicolaides G.L., Long T.C., 1981, AIChE J, 27:33  
 French H.T., Richards A., Stokes R.H., 1979, J.Chem.Thermod., 11:671  
 Gautreaux M.F., Coates J. 1955, AIChE J, 1:497  
 Gibbs R.F., Van Ness H.C., 1972, IEC Fundam. 11:470  
 Hayden J.G., O'Connell J.P., 1975, IEC Proc.Des.Dev., 14:209  
 Hermsen R.W., Prausnitz J.M., Chem.Eng.Sci., 18:485  
 Kolbe B., Gmehling J., 1985, Fluid Phase Equilibria, 23:213  
 Legret D., Richon D., Renon H., 1980 IEC Fundam. 19:122  
 Loblen G.M., Prausnitz J.M., 1982, IEC Fundam., 21:109  
 Maher P.J., Smith B.D., 1979, J.Chem.Eng. Data 24:16  
 Mentzer R.A., Greenkorn R.A., Chao K.C., 1982, J.Chem.Thermod., 14:817  
 Rogalsky M., Rybakiewicz K., Malanowsky S., 1977, Ber.Bunsenges. 10:1070  
 Tomlins R.P., Marsh K.N., 1976, J.Chem.Thermod., 8:1185  
 Van Ness H.C., Abbott M.M., 1978, IEC Fundam., 17:66  
 Willingham C.J., Taylor W.J., Pignocco J.M., Rossini F.D., 1945, J.Research Nat.Bur.Stand., 35:219