Infinite Dilution Activity Coefficients for Oxygenate Systems Determined Using a Differential Static Cell

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A new differential static cell apparatus has been used to measure activity coefficients at infinite dilution for binary systems of water separately with methanol, ethanol, 2-propanol, tetrahydrofuran, and methanol in cyclohexane as a function of temperature, and at 15 °C, we report all binary infinite dilution activity coefficients among methanol–MTBE–cyclopentane and water–2-propanol–ethyl acetate. A description of the apparatus and experimental procedure is given, as well as an error analysis of our experimental data.

Introduction

Infinite dilution activity coefficients are useful for the determination of excess Gibbs free energy model parameters and in designing separation techniques for very dilute systems, such as the production of high-purity reagents and the separation of pollutants from the environment. Since the determination of an infinite dilution activity coefficient by extrapolation of data over the whole composition range usually leads to large errors, direct measurement is preferable. Here we report the direct measurement of infinite dilution activity coefficients using a newly assembled static cell apparatus to measure the equilibrium total pressure at a temperature T above a liquid of known composition, particularly at low pressures (1). The static apparatus is especially suited for the measurement of the equilibrium pressure of systems with large relative volatilities or the possibility of partial miscibility. Also, with a static apparatus measurements are made at equilibrium conditions in contrast to a dynamic apparatus, such as the vapor–liquid still or ebulliometer, which operate at steady state with temperature gradients, and with liquid and condensed vapor holdups. However, solvents and solutes used in a static cell apparatus must be free of impurities, especially any dissolved gases or volatile components which, even at low concentrations, would significantly affect the measured pressure. Therefore, all chemicals must be degassed thoroughly before being used.

The static cell apparatus we used was designed to overcome problems associated with the measurement of activity coefficients at infinite dilution with dynamic equipment (2, 3). In particular, since there is no condensed vapor holdup to alter the composition of gravimetrically prepared mixtures, static cells can be used to measure activity coefficients at infinite dilution of systems with a higher solute volatility than is possible with ebulliometers. Static cells can also be used with solvents with poor boiling properties, such as water (4), and over a large temperature range. Other researchers, such as Alessi et al. (5, 6), have described a differential static apparatus for measuring γ^∞ data and its limitations.

Theory

From the equilibrium relation $\hat{f}_i^L = \hat{f}_i^V$, where $\hat{f}_i$ is the fugacity of species i, Gautreaux and Coates (7) derived the equations to determine activity coefficients at infinite dilution from isothermal pressure–composition measurements. Their expression for the binary activity coefficients at infinite dilution is

$$\gamma_i^\infty = \frac{\phi_i^{(P_j^s)}}{\phi_i^s P_j^s} \frac{\left[P_j^s - \left(1 - \frac{P_j^s v_j^L}{RT} + \frac{P_j^s}{\phi_j^s}\left(\frac{\partial \phi_j^s}{\partial P}\right)_T \right)\left(\frac{\partial P}{\partial x_i}\right)_T^{x_i \to 0} \right]}{\exp[(P_j^s - P_i^s)v_i^L/RT]} \quad (1)$$

Here P_i^s is the vapor pressure of component i, x_i is its mole fraction, ϕ_i^s is the vapor-phase fugacity coefficient of component i at its saturation vapor pressure, ϕ_i^P is the vapor-phase fugacity coefficient of component i at pressure P, and v_i^L is the liquid molar volume of component i. At low pressures and moderate temperatures, so that the virial equation can be truncated at the second virial coefficient, this equation becomes

$$\gamma_i^\infty = \epsilon_i^\infty \frac{P_j^s}{P_i^s}\left(1 + \beta_j \frac{1}{P_j^s}\left(\frac{\partial P}{\partial x_i}\right)_T^{x_i \to 0} \right) \quad (2)$$

where

$$\epsilon_i^\infty = \exp\left[\frac{(B_{ii} - v_i^L)(P_j^s - P_i^s) + \delta_{ij}P_j^s}{RT} \right]$$

$$\beta_j = 1 + P_j^s\left(\frac{B_{jj} - v_j^L}{RT} \right)$$

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$$

and B_{ii} is the second virial coefficient of pure i, B_{ij} is the second virial coefficient corresponding to the i–j interaction, and P_i^s and v_i^L are the pure component vapor pressure and liquid molar volume of component i, respectively.

As will be discussed shortly, the static cell is used to measure $(\partial P/\partial x_1)_T^{x_1 \to 0}$, the limiting slope at infinite dilution in eq 1. Virial coefficients are obtained from experimental data or determined using the Hayden and O'Connell (8) correlation. Vapor pressures of the pure components are either measured or calculated from published Antoine constants (9, 10). From these pieces of information, γ^∞ can be computed. At the conditions of our experiments the ϵ_i^∞ and β_j factors are very close to unity; thus, γ^∞ is essentially determined by the two pure component vapor pressures and from the measured limiting slope.

Equipment and Procedure

Static cells are typically used to measure the equilibrium vapor pressures of mixtures of known composition. Our static
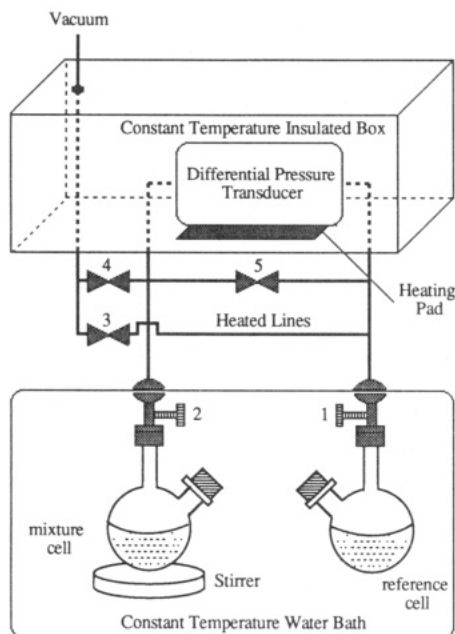
Figure 1. Schematic of the differential static cell equilibrium apparatus.

cell apparatus was designed and constructed specifically to measure the equilibrium total pressure of dilute gravimetrically prepared binary mixtures at constant temperature. By using two static cells, one a reference cell containing only the pure solvent and the other containing the solvent and solute mixture, pressure differences can be measured directly, thereby reducing the error in the pressure difference below that which would be obtained by measuring two absolute pressures. Further, the effect of small temperature fluctuations is minimized.

A schematic diagram of the apparatus and supporting equipment is shown in Figure 1. The static cell apparatus consists of two glass cells each having an injection port, sealed with double septa, for the addition of solvent and solute. The pressure transducer is a Baratron MKS differential pressure transducer, model 221A, with a ±13-kPa range and with an accuracy of 0.01 kPa connected to an MKS PDR-D-1 readout. The transducer is housed in an insulated, temperature-controlled (Sargent thermonitor, model ST) stainless steel box as shown in the figure. The pressure transducer is connected to the glass static cells using Cajon ultratorr fittings welded to stainless steel $^1/_8$-in. tubing, Whitey SS-OKM2 valves, Leybold-Harev vacuum connections, and finally a Swagelok fitting with Teflon ferrules for the glass to stainless steel connection. The Leybold connections allow the removal and replacement of the cells without vaporization or air infiltration. Previous measurements with this equipment (*11*) have proven this apparatus to be reliable, relatively trouble free, and accurate.

Additional equipment used for the static cell measurements consists of a temperature bath that can be raised and lowered so the static cells can be removed from or placed on the static cell manifold. A Neslab Endocal thermostatic water bath was used to control the water bath temperature, and a Flike 2189A thermometry system was used to measure the water bath temperature. This system includes a Y2039 platinum RTD probe with an accuracy of 0.05 °C. The RTD thermometer readout was checked periodically by immersing the probe in an ice–water mixture to check the 0 °C readout, and in boiling water for the 100 °C readout. A vacuum pump was used for the evacuation of the equipment and for the degassing procedure. A Sartorius Model 310A balance was used to weigh the solute and solvent in order to determine the

composition of the mixtures used in our measurements. This balance has a range of 300 g and an accuracy of 2 mg. A separate manifold, also with Leybold fittings, is used to degas the solvents contained in the cells using a vacuum pump and a Bransonic ultrasonic water bath.

The transducer was calibrated using a water manometer over the range of pressure readings. The height of each leg of the water manometer was measured using a cathetometer with an accuracy of ±0.1 mm which is equivalent to ±0.002 kPa in pressure.

Before a series of measurements, all septa were replaced, the glass cells were washed with water and dried in a hot oven overnight, and the water bath was set to the desired temperature. The cell to which solute injections are made, together with the septa and stirring bar, is weighed empty before being attached to the degassing manifold. The static cells are then attached to the degassing apparatus, solvent is added, the cells are then capped, and vacuum is applied to one cell at a time. Once boiling has subsided, about 3–4 min for water, the cells are placed in an ultrasonic bath for further degassing. Again vacuum is applied to one cell at a time for approximately 3–5 min, and this cycle is repeated 4–6 times. Generally the solvent no longer boils after the first couple of cycles in the ultrasonic bath. If the solvent is moderately volatile (i.e., small-chain hydrocarbons), the procedure is similar except that the degassing cycles are much shorter (20–30 s). Alternate freeze–thaw cycles with liquid nitrogen are used for very volatile solvents.

With valves 1 and 2 shut, the cells are removed from the degassing apparatus and the cell which will contain the mixture is weighed and then connected to the manifold containing the pressure transducer. Vacuum is then applied to the transducer for 30 min with valves 1 and 2 to the static cells shut, and valves 3 and 4 open. The zero point of the pressure transducer is recorded. Valves 1 and 2 are then opened while valves 3 and 4 are closed; this isolates the transducer from the vacuum pump and exposes it to the vapor pressure of the solvent. Valve 5, which connects the two static cells, remains closed throughout the measurement. The water bath, now at the set temperature, is raised to cover the cells. The water level of the bath is just below valve 4. The stainless steel tubing above this level is kept hot using heating tape to prevent condensation, the cell contents are stirred, and a reading of the differential pressure is taken every 5 min. The difference between the vapor pressures of the solvent in the two cells is typically within ±0.05 kPa of the zero point. The vapor pressure of the solvent in the reference cell is found by leaving valves 1 and 4 open and valves 2 and 3 closed, and recording the transducer readings (vapor pressure of reference cell) every 5 min for 30 min.

After the vapor pressure measurements, valves 3 and 4 are opened, and valves 1 and 2 are closed. The mixture static cell is prepared for the solute injection by closing valve 2, disconnecting the cell, and replacing it in the hot water bath for about 10 min so that the vapor pressure in the cell is about 1 atm. In this way, air infiltration during the injection of the solute into the cell is eliminated. A Hamilton gas-tight syringe, type 1427, is then used to withdraw a quantity of previously degassed solute from a degassing cell (which is identical to the measurement cells) to inject into the mixture cell. The syringe containing the solute is weighed on the balance. The cell is removed from the hot water bath and inverted; the solute is then injected, and the empty syring is weighed after the injection. The cell is cooled to the water bath temperature while being shaken, and then is once again attached to the transducer. Valve 3 is opened to vacuum for approximately 10 min, and then this valve is closed and valve 2 opened. The pressure difference is then recorded every 5 min for 30–
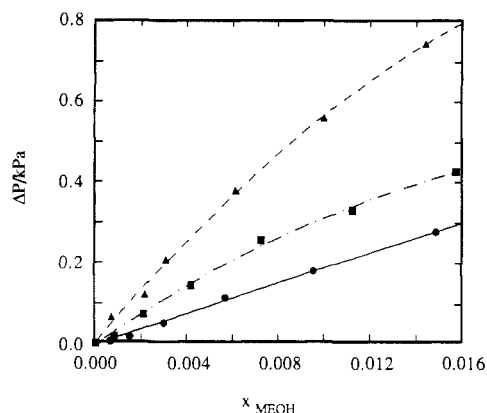
Figure 2. Experimental data and second-order polynomial fit, eq 3, of the differential pressure versus composition for methanol (1) + water (2): ●, 20 °C; ■, 30 °C; ▲ 40 °C.

45 min until it is constant. The injection procedure is repeated five additional times, doubling the solute volumes with each injection. Solute quantities used were approximately 10 μL for the first solute injection and 200 μL for the last (the injections were 2 or 3 times larger when the relative volatility was less than 5). A 10-μL injection corresponds to approximately 0.1 wt % (0.001 wt fraction) solute in solvent.

Chemicals. The purity of the solvent is crucial to the accurate determination of infinite dilution activity coefficients from static cell measurements. The highest purity solvents available were used in all experiments. Cyclohexane and tetrahydrofuran of purity 99.9% from Aldrich Chemicals were used as received. Methanol and 2-propanol purchased from Aldrich Chemicals with purities of 99.5% or better and 200-proof ethanol purchased from U.S. Industrial Chemicals Corp. (Tuscola, IL) were also used as received. Ethyl acetate was purchased from Aldrich Chemicals under their Gold Label with purity of 99.9% and used as received. The water used was distilled, filtered, and deionized.

Data Analysis and Results

Figure 2 is an example of the change in pressure as a function

of the liquid mole fraction charged. These data were fit to the second-degree polynomial

$$\Delta P = a + bx_i + cx_i^2 \qquad (3)$$

By using this polynomial, an accurate value of the limiting slope $(\partial P / \partial x_i)_{T}^{x_i \to 0}$ can be obtained which is not influenced by any remaining transducer offset ΔP or by curvature of the pressure versus mole fraction curve which occurs at higher mole fractions of solute. The value of $(\partial P / \partial x_i)_{T}^{x_i \to 0}$ is then equal to the value of the parameter b. The data were also fit to a third-degree polynomial; however, since the data were approximately linear, the limiting slopes using different order polynomials gave γ_i^{∞} values which differed by less than 1%. Also, the use of higher order polynomials did not give significant improvements in the standard deviation over that obtained using a second-order polynomial fit, which fit the data to within the experimental error.

The limiting slopes were used in eq 2 to determine the activity coefficients at infinite dilution. In these calculations, the measured pure component vapor pressures were used, and the vapor-phase nonidealities at low pressure were accounted for using a truncated virial equation of state. Experimental data or the generalized method of Hayden and O'Connell (8) was used to determine these second virial coefficients; other pure component data were taken primarily from Reid et al. (9) and Boublík et al. (10). The infinite dilution activity coefficients and pressure-composition slopes are given in Table I.

There are few direct measurements of infinite dilution activity coefficients with which we can compare. Considerable scatter is evident in the infinite dilution activity coefficients of ethanol in water which have been reported as 6.51 at 20 °C (12), 4.74 at 24.3 °C (13), 3.27 at 25 °C (14), and 6.15 at 30 °C (12); our values are 4.81 at 20 °C and 5.17 at 30 °C. Values for methanol in water have been reported to be 2.69 at 20.0 °C (12), 2.12 at 24.3 °C (13), 1.65 at 25 °C (14), and 2.20 at 27.3 °C (15) compared to our values of 1.68 at 20 °C and 1.77 at 30 °C. Finally infinite dilution activity coefficients for 2-propanol in water have been reported to be 13.62 at 80 °C and 14.00 at 100 °C; we find 12.9 at the much lower temperature of 15 °C. By regressing vapor-liquid equilibrium

Table I. Measured Infinite Dilution Activity Coefficients and Limiting Slopes

mixture	T/°C	γ_i^{∞}	$(\partial P / \partial x_1)_{T}^{x_1 \to 0}$/kPa	$G_1^{EX}(x_1 \to 0)$/ (kJ/mol)	$S_1^{EX}(x_1 \to 0)$/ (J/(mol·K))	$H_1^{EX}(x_1 \to 0)$/ (kJ/mol)
methanol (1) + water (2)	20.0	1.68 ± 0.12	14.6 ± 1.6	1.264		
	30.0	1.77 ± 0.10	22.1 ± 1.3	1.489	−21.7	−5.10
	40.0	1.92 ± 0.08	32.1 ± 1.3	1.698		
ethanol (1) + water (2)	10.0	4.38 ± 0.21	5.5 ± 1.0	3.477		
	20.0	4.81 ± 0.19	17.0 ± 0.9	3.828		
	30.0			4.052	−22.4	−2.75
	40.0	5.17 ± 0.16	31.7 ± 0.7	4.277		
	60.0	5.59 ± 0.12	41.7 ± 0.7	4.767		
tetrahydrofuran (1) + water (2)	20.0	16.6 ± 0.2	68.9 ± 3.7	6.847		
	35.0	23.5 ± 0.2	149.0 ± 5.0	8.088	−84.3	−17.9
	50.0	32.8 ± 0.5	259.4 ± 7.3	9.377		
methanol (1) + cyclohexane (2)	10.0	118.8 ± 6.8	881.0 ± 50.0	11.247		
	20.0	77.8 ± 4.0	1040 ± 55.0	10.612	14.3	15.3
	40.0	63.7 ± 3.0	2210 ± 110	10.816		
methanol (1) + MTBE (2)	15.0	3.75 ± 0.07	16.36 ± 0.65	3.167		
MTBE (1) + methanol (2)	15.0	6.05 ± 0.11	115.8 ± 2.32	4.312		
methanol (1) + cyclopentane (2)	15.0	169.5 ± 7.5	1646.1 ± 74	12.30		
cyclopentane (1) + methanol (2)	15.0	16.2 ± 0.21	445.4 ± 5.9	6.672		
cyclopentane (1) + MTBE (2)	15.0	1.69 ± 0.02	26.75 ± 0.5	1.257		
MTBE (1) + cyclopentane (2)	15.0	3.87 ± 0.12	52.3 ± 2.5	3.242		
2-propanol (1) + water (2)	15.0	12.9 ± 0.57	36.67 ± 1.7	6.127		
water (1) + 2-propanol (2)	15.0	5.72 ± 0.11	8.12 ± 0.18	4.178		
2-propanol (1) + ethyl acetate (2)	15.0	4.63 ± 0.07	6.11 ± 0.21	3.672		
ethyl acetate (1) + 2-propanol (2)	15.0	3.55 ± 0.08	24.6 ± 0.61	3.035		
ethyl acetate (1) + water (2)	15.0	63.9 ± 1.96	483.3 ± 5.8	9.960		
water (1) + ethyl acetate (2)	15.0	18.1 ± 0.17	23.0 ± 0.32	6.938		

data over the whole composition range, Gmehling et al. (*16*) report infinite dilution activity coefficients in the DECHEMA Chemistry Data Series. For methanol in water, values of 1.60 and 1.87 are reported at 20 °C, 2.05 at 39.9 °C, and 1.56, 1.93, and 1.94 at 50 °C which are in general agreement with our values of 1.68 at 20 °C, 1.77 at 30 °C, and 1.92 at 40 °C. For ethanol in water they report 4.09 at 20 °C, 4.46 at 30 °C, and 4.17, 5.06, and 5.07 at 40 °C which is to be compared with our values of 4.81 at 20 °C and 5.17 at 40 °C. Given the scatter in the direct measurements of others, and the uncertainty in the extrapolations to infinite dilution from VLE data, we conclude that there is generally good agreement between the data we obtained here and that reported by others.

For an error analysis of our apparatus, the accuracy used for each piece of equipment was as reported by the vendor or based on our experience. The solvents were gravimetrically measured with an accuracy of ±2 mg and solute injections with an accuracy of ±1 mg. The error in the differential pressure measurement is ±0.02 kPa. Because of the very low density of the vapor and the magnitude of the vapor volume, the static cell apparatus does not require a correction for the vapor-phase holdup for systems with relative volatilities below 100. This is a major advantage over other methods of determination of infinite dilution activity coefficients. For the purpose of the error analysis, the vapor phase is assumed to be ideal so that eq 2 reduces to

$$\gamma_1^{\infty} = \frac{P_2^{s}}{P_1^{s}}\left(1 + \frac{1}{P_2^{s}}\left(\frac{\partial P}{\partial x_1}\right)_T^{x_1 \rightarrow 0}\right) \qquad (4)$$

Rearranging eq 4, the isothermal pressure–composition infinite dilution slope from a static cell measurement is

$$(\partial P/\partial x_1)_T^{x_1 \rightarrow 0} = (\alpha_1^{\infty} - 1)P_2^{sat} \qquad (5)$$

where the infinite dilution relative volatility is

$$\alpha_1^{\infty} = \left(\frac{y_1/x_1}{y_2/x_2}\right)_{x_1 \rightarrow 0} = \left(\frac{\gamma_1 P_1^{sat}}{\gamma_2 P_2^{sat}}\right)_{x_1 \rightarrow 0} = \frac{\gamma_1^{\infty} P_1^{sat}}{P_2^{sat}}$$

The pure component vapor pressures and their temperature derivatives can be determined using the Antoine equation. From eq 4 we can write the following expressions for the absolute and relative errors in the infinite dilution activity coefficient:

$$\delta\gamma_1^{\infty} \simeq \frac{1}{P_1^{sat}}\left(\delta\left(\frac{\partial P}{\partial x_1}\right)_T^{x_1 \rightarrow 0}\right) \qquad (6)$$

and

$$\frac{\delta\gamma_1^{\infty}}{\gamma_1^{\infty}} \simeq \frac{1}{P_2^{sat}}\frac{\delta(\partial P/\partial x_1)_T^{x_1 \rightarrow 0}}{\alpha_1^{\infty}} \qquad (7)$$

Also, we can express the error in the infinite dilution slope as

$$\delta\left(\frac{\partial P}{\partial x_1}\right)_T^{x_1 \rightarrow 0} = \frac{\delta P + \delta x_1(\partial P/\partial x_1)_T^{x_1 \rightarrow 0}}{x_1} \qquad (8)$$

For our measurements $\partial P = \pm 0.6$ kPa and $\partial x = \pm 0.005$, which we use in the equation above. The magnitude of the acceptable relative error in γ^{∞} determines the range of relative volatilities that can be studied in a static cell.

Results of the error analysis indicate that the infinite dilution activity coefficient measurement becomes more accurate at higher solvent vapor pressures and a high relative volatility (greater than 5). Though if the solute relative

volatility becomes too high (greater than several hundred), then a correction is needed to account for the difference between the gravimetrically prepared composition of the liquid and its actual composition due to evaporation of the solution into the vapor space. In our equipment the vapor space, which is mostly in the transducer, is about half of that of the liquid. The results of the error analysis on both the limiting slopes and the activity coefficients computed using eq 8 are given in Table I.

Finally, since we have measured some of the infinite dilution activity coefficients as a function of temperature, we can compute other thermodynamic properties at infinite dilution as follows:

$$G_1^{EX}(x_1 \rightarrow 0, T) = RT \ln \gamma_1^{\infty}(T)$$

$$S_1^{EX}(x_1 \rightarrow 0, T) = -\frac{\partial G_1^{EX}(x_1 \rightarrow 0, T)}{\partial T}\bigg|_P \approx -\frac{\Delta G_1^{EX}(x_1 \rightarrow 0, T)}{\Delta T}$$

and

$$H_1^{EX}(x_1 \rightarrow 0, T) = G_1^{EX}(x_1 \rightarrow 0, T) + TS_1^{EX}(x_1 \rightarrow 0, T)$$

As numerical differentiation is involved in the calculations of S_1^{EX} and H_1^{EX}, we report these values at a single intermediate temperature in Table I, and G_1^{EX} at all temperatures.

Conclusions

We have used a new static cell apparatus to measure infinite dilution activity coefficients for a number of systems as a function of temperature. From these data we have computed the partial molar mass enthalpy, entropy, and Gibbs free energy at infinite dilution. We have also done an error analysis of this new equipment.

Acknowledgment

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