A Dew Point Technique for Limiting Activity Coefficients in Nonionic Solutions

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A new measurement technique for activity coefficients at infinite dilution has been developed involving the construction of a very dilute vapor phase and the accurate determination of its dew point. This method is especially applicable to systems of low solute relative volatility, precisely where other methods such as differential ebulliometry and headspace gas chromatography become less precise. Data are reported for γ^∞ for N, N-dimethylformamide, dimethylsulfoxide, and N-methyl pyrrolidone in water over a range of temperatures.

Introduction

Limiting activity coefficients, γ^∞, are useful in obtaining parameters for excess Gibbs energy models and thus can be used to predict phase behavior. This property is also a means of evaluating intermolecular interactions with the purpose of understanding and modeling solution behavior. Several good techniques available for measuring this property include dynamic gas chromatography (Pescar and Martin, 1996; Shaffer and Daubert, 1969), gas stripping (Leori et al., 1977; Richon and Renon, 1980; Richon et al., 1980), differential ebulliometry (Scott, 1986; Trampe and Eckert, 1990), and headspace chromatography (Hassam and Carr, 1985). While these measurement methods allow us to investigate a wide variety of solutions, they have difficulty measuring systems with very small relative volatilities. Gas chromatography and gas stripping are unable to measure systems with relative volatilities less than unity. Differential ebulliometry has problems measuring systems with relative volatilities less than ~0.3 due to mathematical analysis of the data reducing to a small difference between large numbers. When the relative volatility is low, the vapor-phase composition becomes difficult to measure accurately in headspace chromatography.

We present a new technique that is especially useful for measuring systems with low relative volatility. The technique is analogous to the differential ebulliometer method and involves measuring the change in temperature of the dew point of a vapor solvent when a dilute amount of solute is added. Values of γ^∞ of *N*, *N*-dimethylformamide (DMF) in water were measured by this method and compared with those measured by differential ebulliometry and headspace chromatography.

We also present γ^∞ data for the systems dimethylsulfoxide (DMSO) and *N*-methyl pyrrolidone (NMP) in water over a range of temperatures. Water is a unique solvent, and γ^∞ values of solutes in water can be as low as 0.1 and as large as 10^6 or even 10^8. This technique allows us to study the low end of this range. Data over such a wide range is useful in the development of predictive models for γ^∞. Dilute aqueous solutions are also of great interest in the areas of biotechnology and environmental control.

Theory

The expression relating γ_1^∞ of a solute (1) in a solvent (2) to the change in dew point temperature $(\partial T/\partial y_1)_P^\infty$ at constant pressure is derived in a similar fashion to that of the ebulliometer technique (Gautreaux and Coates, 1955):

$$\gamma_1^\infty = \frac{(P_2^S)^2\phi_1}{\phi_1^S P_1^S \exp\left[\frac{\nu_1(P_2^S - P_1^S)}{RT}\right]\left[P_2^S - P_2^S\frac{\partial\phi_2}{\partial y_1} + \left(\frac{\partial T}{\partial y_1}\right)_P^\infty\left(\frac{\partial P_2^S}{\partial T}\right)\left(1 - \frac{\nu_2 P_2^S}{RT}\right)\right]} \tag{1}$$

If we disregard the fugacity coefficient terms and the Poynting

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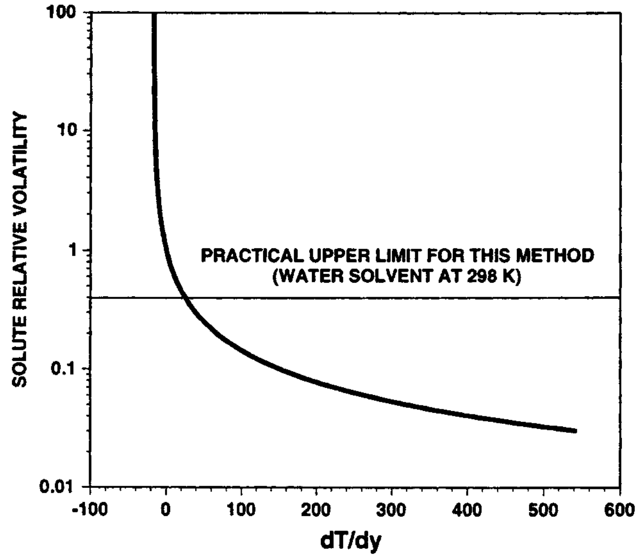

Figure 1. Dew point temperature change with composition, $(\partial T/\partial y_1)_P^\infty$, vs. solute relative volatility, α, for the water solvent system at 298 K.

correction, all of which are generally of little significance at low pressures, this equation reduces to:

$$\gamma_1^\infty = \frac{(P_2^S)^2}{P_1^S\left[P_2^S + \left(\frac{\partial T}{\partial y_1}\right)_P^\infty \left(\frac{\partial P_2^S}{\partial T}\right)\right]} \tag{2}$$

The relative volatility of a solute infinitely dilute in a solvent is essentially given by:

$$\alpha = \frac{P_1^S \gamma_1^\infty}{P_2^S} \tag{3}$$

By substituting Eq. 3 into Eq. 2 we can obtain an expression relating the measured $(\partial T/\partial y_1)_P^\infty$ to the relative volatility of the solute in the solvent:

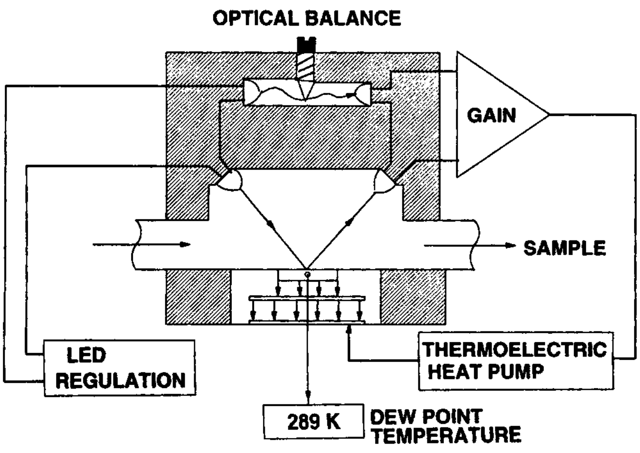

Figure 2. Dew point sensor.

$$\left(\frac{\partial T}{\partial y_1}\right)_P^\infty = \frac{P_2^S}{\left(\frac{\partial P_2^S}{\partial T}\right)} \frac{(1-\alpha)}{\alpha} \tag{4}$$

Note that this expression depends only on the solvent and the temperature; the solute properties are all contained in α. When water is the solvent at 298 K, this expression becomes:

$$\left(\frac{\partial T}{\partial y_1}\right)_P^\infty = 16.8 \frac{(1-\alpha)}{\alpha} \tag{5}$$

This equation is illustrated in Figure 1. As α becomes very large, $(\partial T/\partial y_1)_P^\infty$ quickly becomes small, becoming 0 at $\alpha = 1$ and approaching -16.8 for large relative volatilities. Since we are working at infinite dilution, typical Δy values are 0.001 mole fraction or less. The upper volatility limit is set by the temperature measurement sensitivity, which for this experiment is 0.01 K. Thus, the upper volatility limit for this case (water solvent, 298 K) is approximately 0.4. As the run temperature increases, this limit can be raised, but only slightly.

As α becomes small, however, $(\partial T/\partial y_1)_P^\infty$ becomes very large. The only limitation in low relative volatility is that the difference in the vapor pressure of the solute and solvent cannot be so large that the vapor phase cannot be physically constructed. This technique applies best for systems in which the vapor pressure of the solute is considerably less than that of the solvent, especially for systems that show negative deviations from Raoult's law due to solvation in the mixture.

Apparatus

The experiment revolves around a General Eastern model D2 chilled mirror dew point sensor, a commercial device used primarily to measure humidity of gas samples, as shown in Figure 2. The sensor works by flowing a vapor sample over a thermoelectrically cooled platinum mirror. A high-intensity, solid-state, light-emitting diode is reflected off the mirror surface, and the intensity of the reflected light is monitored. As the mirror is cooled, dew begins to form on the mirror surface, scattering the light and reducing the reflected intensity. The temperature of the mirror is adjusted and controlled by the General Eastern Hygro-M3 electronics unit to maintain a constant thin layer of dew on the surface. The mirror temperature thus is held at the dew point of the sample and is measured with a precision platinum resistance thermometer embedded just beneath the mirror surface. The temperature measurement has a repeatability of ±0.02 K. The sensor can measure dew point temperatures ranging from 350 K to approximately 40 K lower than the sensor body temperature.

The sensor is used in the experimental setup shown in Figure 3. Pure solvent or a solution of known composition is pumped using a Cole-Parameter Masterflex L/S variable speed peristaltic pump (model 7520-35) through a 50-μm-ID bulk fused silica capillary tubing of length 0.15 to 0.51 m, depending on the system pressure. The capillary tubing assures that liquid is being pumped and not "pulled" into the system due to the pressure drop, thus assuring a relatively constant flow rate. The capillary extends approximately 5 cm into a preheated section consisting of 0.635-cm-ID copper tubing approximately 0.6 m long wrapped by heating tape, where the liquid is completely vaporized. The vapor then flows through the sensor, which is maintained at a temperature higher than the dew point temperature by a Blue M Stabil-Therm gravity convection oven (model OV12A) stable to ±0.2°C. The vapor exits the oven and is then condensed and collected in a water-cooled condenser or an ice trap.

The entire system is maintained at constant pressure by a MKS high-accuracy Baratron system, capable of resolution of 1.3 Pa. It consists of a type 390 sensor head, a type 270 C-5 electronics unit, and a type 250B pressure controller with a 248A control valve of range 100 std. $cm^3 \cdot min^{-1}$. A 50-l ballast tank is included to minimize pressure fluctuations. The system pressure is controlled to 6.7 Pa. The dew point temperature and system pressure are collected with a data acquisition system in a personal computer.

Materials

The water used in this experiment was Aldrich HPLC-grade purity. The solutes were obtained from Aldrich with stated purity of >99% and checked with gas chromatography. The water content of the solutes was also measured by a Mitsubishi Kasei Karl Fisher device and found to be negligible. When measuring γ^∞ for water infinity dilute in organic compounds, the water content of the organic can be a large problem.

Procedure

Solutions of the solutes in water were constructed gravimetrically and stirred for ~1/2 to 1 hour with a magnetic stirrer. The solutions of DMF in water had compositions ranging from 0.1 to 0.5 mol % DMF. Due to the very low relative volatilites of DMSO and NMP in water (and thus large dT/dy values), even more dilute solutions were required. NMP solutions had compositions from 0.05 to 0.1 mol % NMP, and solutions of 100 to 500 ppm by mole of DMSO were made by further diluting a 0.5 mol % DMSO solution. Once the solutions are made, they can be used for a series of measurements over a range of temperatures.

The oven temperature is set so that the sensor is maintained at approximately 5 K above the expected dew point and held fairly constant (±0.2 K). The preheat section is heated to 40-60°K hotter than the dew point temperature. Although the temperature of the preheat section is not critical, it must be hot enough to vaporize totally the solution. If it is too hot the sensor control was found to be affected. The mirror surface is cleaned with acetone before the pressure is set to give the desired temperature.

At each temperature a liquid flow rate must be determined. General Eastern recommends a vapor flow rate between 5.7-140 L/h STP through the dew point sensor. We found, however, that at flow rates larger than 5.7 L/h STP the sensor control and the repeatability of the dew point measurement were affected. Vapor flow rate in general was found not to affect the dew point measurement except at temperatures less than 308 K. Therefore, the largest flow rate that gave consistent measurement (approximately 2.8 L/h STP) was used. The liquid flow rate required to give this vapor flow rate is determined, and the pump is set. The capillary length is determined by the Hagen-Poiseuille law.

Pure solvent is pumped through the system for approximately 10 min. The cooling current in the sensor mirror is switched on, and the mirror is cooled to the dew point temperature. When the sensor signals that it has control of the dew layer on the mirror surface, the temperature of the mirror and the system pressure are recorded for approximately 10 min. The cooling current is then disabled, and the pure solvent is replaced with a solution. The procedure is repeated until four or five solutions of increasing solute concentration are measured. Finally, pure solvent is measured again. The entire process requires 4-5 hours.

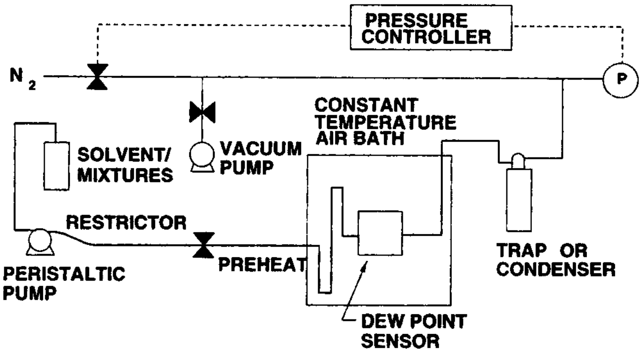

Figure 3. Overall design of the system used to measure limiting activity coefficients by dew point measurement.

Data Reduction

A typical dew point measurement is shown in Figure 4. By using the temperature derivative of the vapor pressure expression for water we can correct the dew point temperature for fluctuations caused by pressure changes. When these corrections are made, fluctuations in the dew point temperature are between 0.002 and 0.1 K. The temperature and pressure values are averaged for each measurement of pure solvent and solutions. The pressure for the first pure solvent measurement is taken as the system pressure. All the dew point temperature measurements for the solutions and the final pure solvent are corrected to this pressure. The ΔT values are found by taking the difference between each corrected solution dew point tem-

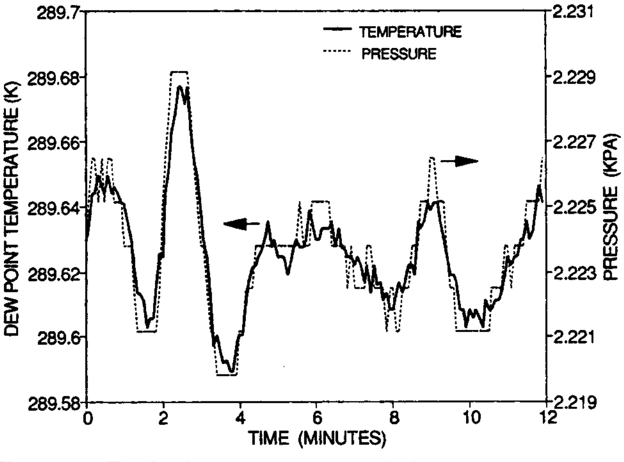

Figure 4. Typical measurement of the dew point temperature and pressure for pure water.

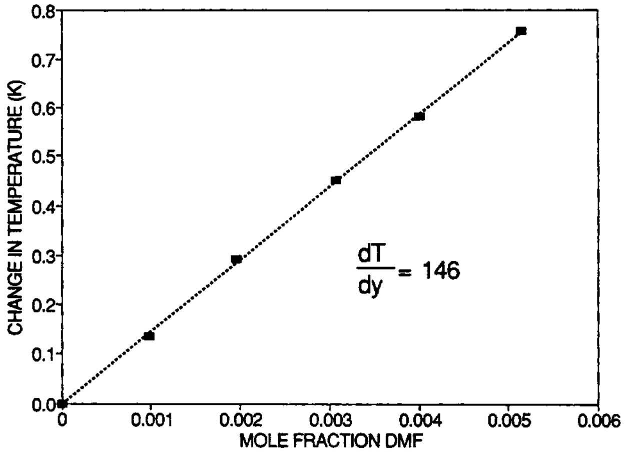

Figure 5. Sample ΔT vs. y data for DMF in water at 298 K.

perature and the first pure solvent dew point measurement. A sample plot of ΔT vs. composition is shown in Figure 5. The temperature difference between the two pure solvent measurements is taken as a check and was always less than 0.02 K.

The experimental $\Delta T - y$ data are fit to various empirical equations:

$$\Delta T = Ay_1 + By_1^2 \qquad \text{(quadratic)} \tag{6}$$

$$\Delta T = Ay_1 + By_1^2 + Cy_1^3 \qquad \text{(cubic)} \tag{7}$$

$$\frac{1}{\Delta T} = \frac{A}{y_1} + \frac{B}{y_1 y_2} \qquad \text{(van Laar)} \tag{8}$$

In the first two expressions $(\partial T/\partial y_1)_P^\infty = A$, and in the third expression $(\partial T/\partial y_1)_P^\infty = 1/B$. The fits are generally close to linear and usually differed by less than 7%. The value of $(\partial T/\partial y_1)_P^\infty$ is taken from the expression that has the smallest standard deviation of fit given by:

$$\sigma = \left[\frac{\Sigma(\Delta T_{\text{calc}} - \Delta T_{\text{exp}})^2}{(n-N)}\right]^{1/2} \tag{9}$$

Table 1. Experimental γ^∞ Values in Water

Solute	Temp. K	Experimental γ^∞
N,N-dimethylformamide	289.4	0.58±0.03
	298.0	0.65±0.11
	307.8	0.81±0.08
	317.9	0.95±0.11
	328.3	1.11±0.04
	338.0	1.30±0.40
dimethylsulfoxide	298.8	0.09±0.02
	308.4	0.10±0.002
	318.0	0.12±0.017
	328.4	0.135±0.015
	337.9	0.17±0.004
N-methyl pyrrolidone	298.8	0.37±0.014
	308.4	0.60±0.09
	318.0	0.86±0.15
	328.4	1.13±0.03
	337.9	1.39±0.20

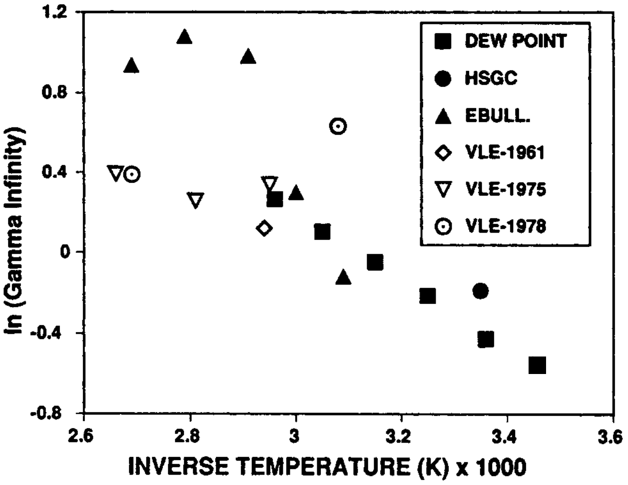

Figure 6. Comparison of γ^∞ values for DMF in water measured by the dew point method with values obtained by other sources.

HSGC = Headspace Gas Chromatography data of Dallas (1993)
Ebull = Ebulliometry data of this study and Bergmann and Eckert (1991).
VLE = Data form Golubkov et al. (1975); Misheneva et al. (1978); Susarev (1961).

where n is the number of data points and N is the number of adjustable parameters in the equation. This $(\partial T/\partial y_1)_P^\infty$ value is then used in Eq. 1 to obtain γ^∞. Since this experiment relies on a difference in temperatures, there is no need for temperature calibration. Also, since this is a vapor-phase and flow experiment, there is no need to make corrections in the vapor-phase composition.

As a final check, the entire data reduction is repeated with the final pure solvent measurement taken as the reference. The γ^∞ value calculated from this analysis differed from the first γ^∞ by less than 10% and often less than 5%. The final γ^∞ value is taken as the average of the two values.

Results

The system DMF infinitely dilute in water was measured at 289-338 K; experimental γ^∞ values are shown in Table 1. The γ^∞ value at each temperature was measured at least twice, and error estimates are based on the replicate data. A plot in ln γ^∞ vs. inverse temperature is shown in Figure 6 along with γ^∞ values obtained from other sources. Because of strong polar forces and hydrogen bonding, this system is not regular, but the dew point data appear linear over the temperature range studied; however, extrapolation outside the range could be dangerous.

At 298 K the relative volatility of this system is approximately 0.1, an area where the dew point technique best applies. This low volatility makes γ^∞ difficult to obtain by the headspace technique due to difficulties in measuring a very small vapor composition. The headspace value of Dallas (1993) could be slightly high due to transfer losses (Carr, 1992). The dew point measurements were also compared with ebulliometer measurements reported previously (Bergmann and Eckert, 1991) along with new measurements at higher temperatures (at 358 K $\gamma^\infty = 3.0 \pm 0.2$; at 373 K $\gamma^\infty = 2.6 \pm 0.2$). The ebulliometry method is also less accurate in the low relative volatility region

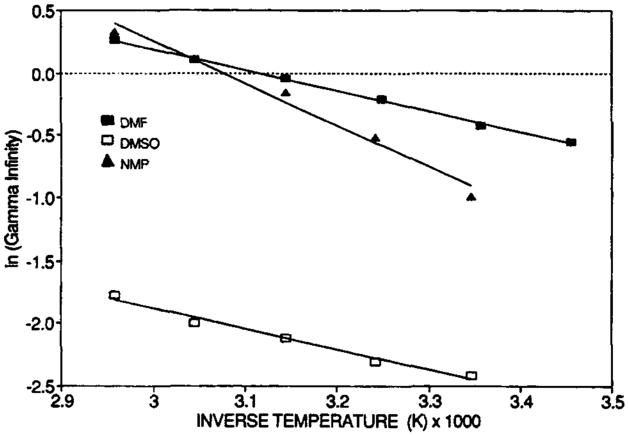

Figure 7. ln γ^∞ vs. $1/T$ for DMF, DMSO and NMP.

where the dew point method works best. The lowest temperature values, however, appear consistent with the dew point values. The behavior of the higher temperature measurements has been replicated and is unusual. It may be due to the complex hydrogen bonding in a system with both association and solvation.

Values of γ^∞ may also be obtained by extrapolating traditional vapor-liquid equilibrium (VLE) data. However, extrapolating VLE data can produce large uncertainties in γ^∞, especially for complex hydrogen bonded systems. For example, extrapolating the DMF-H_2O VLE data of Golubkov et al. (1975) using the Margules equation gives a γ^∞ of 1.86, while the Wilson equation gives a γ^∞ of 1.4. Nonetheless, the classical VLE data have been extrapolated using the Wilson equation, as shown on Figure 6. Compared with all other reported data, the dew point data show the most internal consistency.

Values of γ^∞ for DMSO and NMP from 298-338 K are given in Table 1. The errors were estimated from the difference between the different fitting routines for $(\partial T/\partial y_1)_P^\infty$. All the γ^∞ data measured are shown in Figure 7. Only the NMP system shows any curvature; however, this variation is still within the error of the data. The slope of these data yields the partial molar excess enthalpy at infinite dilution, $h_i^{E\infty}$. Using a linear fit of the data $h_i^{E\infty}$ was estimated for these systems and given in Table 2. The temperature ranges studied here are small, however, and it is preferable to measure this quantity directly by using a technique such as asymmetric isothermal flow calorimetry (Trampe and Eckert, 1990).

Table 2. Experimental Excess Enthalpy at Infinite Dilution Values, $h_i^{E\infty}$ Calculated from Experimental γ^∞ Values in Water

Solute	$h_i^{E\infty}$ (kJ/mol)
N, *N*-dimethylformamide	-13.5 ± 5
dimethylsulfoxide	-13.6 ± 7
N-methyl pyrrolidone	-28.0 ± 4

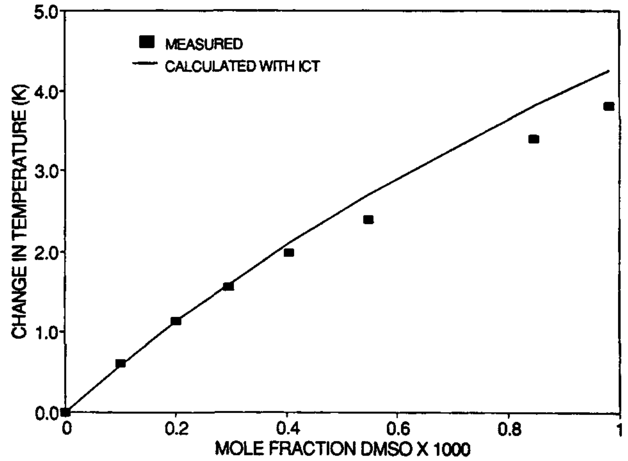

Figure 8. Fit of measured $\Delta T-y$ data with ideal chemical theory for the DMSO-H_2O system at 308 K.

All three systems studied had γ^∞ values less than unity over part or all of the temperature region studied. These low γ^∞ values are undoubtedly due to the solvation occurring in the mixture. In fact, even at concentrations of DMSO in water as low as 100 to 500 ppm by mole, there was noticeable curvature in the measured $\Delta T-y$ values as seen in Figure 8. Treating the system as a simple solvation reaction of the form:

$$A+B\rightleftharpoons AB \tag{10}$$

the measured γ^∞ value at 308 K was used to find the equilibrium constant K_{AB} from ideal chemical theory (Alger and Eckert, 1983), neglecting all other physical and chemical interactions in the dilute solution.

$$\gamma^\infty=\frac{1}{K_{AB}+1} \tag{11}$$

The dew point data for DMSO-H_2O at 308 K were fit with K_{AB} as the single adjustable parameter, and the results are compared with the measured values in Figure 8. Ideal chemical theory predicts the same curvature but to a lesser degree as the solution becomes more concentrated and other interactions become important.

Extension of the Method

The dew point sensor used in this experiment is especially suited for water solvent systems. Water, due to its large surface tension, condenses dropwise on the platinum mirror surface, and the dew point can be easily detected. Other organic chemicals condense filmwise, making detection difficult. This technique can be adapted to measure γ^∞ of solutes in organic solvents by coating the mirror surface with a low energy substance, a perfluoroalkane, for example.

Another advantage of the dew point experiment is that it is easily run at elevated pressures. The current instrument is rated at 1,100 kPa but could be extended easily to much higher pressures with modification of the sensor. In other γ^∞ methods, high pressure decreases the precision of the measurements; in ebulliometry and headspace gas chromatography, the vapor holdup becomes an unacceptable correction at elevated pressures. In the dew point method, since the vapor phase is the phase constructed, no such limitation exists. The method is also extensible to measuring γ^∞ at low temperatures. Thus, this technique could be used to investigate systems that are gases at room temperature.

The dew point experiment consists primarily of commercially available equipment that is easy to assemble and duplicate. Finally, it should be recognized that since this experiment is good for measuring γ^∞ for systems of low solute relative volatility, it is a complimentary technique for such methods as dynamic gas chromatography and gas stripping which can only measure γ^∞ for solutes that are more volatile than the solvent.

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Notation

α = relative volatility
γ_i^∞ = activity coefficient at infinite dilution
$h_i^{E\infty}$ = partial molar enthalpy at infinite dilution
ϕ_i = fugacity coefficient of the vapor
ϕ_i^S = fugacity coefficient at saturation pressure
P = total pressure
P_i^S = saturation pressure
R = gas constant
T = temperature
v_i = liquid molar volume
x_i = composition

Subscripts

1 = solute
2 = solvent

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