Limiting Activity Coefficients of Diols in Water by a Dew Point Technique

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Limiting activity coefficients for 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol and 2,3-butanediol in water were measured over a range of temperatures (297–348 K). The recently developed dew point technique used in this investigation is especially suitable to this type of system with very low relative volatility (*e.g.*, <0.5), where other methods are inapplicable. The experimental results were compared with extrapolated vapor–liquid equilibrium (VLE) data, demonstrating the inadequacy of extrapolating VLE data to γ^∞ for complex hydrogen-bonded systems. A one-parameter Wilson equation was used to characterize the results and to estimate γ^∞ for water in the diols. Partial molar excess enthalpies at infinite dilution were estimated from the temperature derivative of the limiting activity coefficients. The results are discussed in terms of inter- and intramolecular hydrogen bonding.

Introduction

Knowledge of limiting activity coefficients, γ^∞, can be crucial for the accurate design of any separation process as well as for the characterization of solute–solvent intermolecular interactions. Experimental techniques for the direct determination of γ^∞ (*1*) include dynamic gas chromatography (*2, 3*), gas stripping, also called the dilutor method (*4–6*), differential ebulliometry (*7, 8*), and headspace chromatography (*9*). Each of these methods applies best for a particular range of relative volatility, but the dew point technique (*10*) is the only technique available for the accurate measurement of systems with very low relative volatilities (*e.g.,* <0.5).

The unique structure and hydrogen-bonding characteristics of water make it a particular challenge for γ^∞ correlation and prediction (*11–15*). Values of γ^∞ can range from below unity to as high as 10^6 or even 10^8 for aqueous systems. The study of diols in water offers the potential to investigate the competitive effects of both inter- and intramolecular hydrogen bonding of a solute in water. Moreover, diols are also of interest in areas such as refrigeration, hydrodynamics (*i.e.*, raw material for hydraulic brake fluids), and paints (*e.g.*, production of ink, or as solvents for paint manufacturing), and even in various plastic industries (*16*).

This investigation measured values of γ^∞ for 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, and 2,3-butanediol in water over a range of temperatures (297–348 K) using a dew point technique.

Theory

The dew point method gives γ_2^∞ of a solute (2) in a solvent (1) (*10*):

$$\gamma_2^\infty = (P_1^s)^2\phi_2/\phi_2^s P_2^s \exp\left(\frac{v_2(P_1^s - P_2^s)}{RT}\right) \times \left(P_1^s - P_1^s\frac{\partial\phi_1}{\partial y_2} + \left(\frac{\partial T}{\partial y_2}\right)\left(\frac{\partial P_1^s}{\partial T}\right)\left(1 - \frac{v_1P_1^s}{RT}\right)\right) \quad (1)$$

We use the Hayden and O'Connell method (*17*) for calculating virial coefficients for vapor-phase nonidealities. In any event, these corrections are minor, especially at low pressures, and this equation reduces to

$$\gamma_2^\infty = \frac{(P_1^s)^2}{P_2^s\left(P_1^s + \left(\frac{\partial T}{\partial y_2}\right)\left(\frac{\partial P_1^s}{\partial T}\right)\right)} \quad (2)$$

Experimental Apparatus

The experimental apparatus is presented in Figure 1. Pure solvent or a solution of known composition is pumped using a Cole-Parmer Masterflex L/S variable speed peristaltic pump (model 7520-35) through a 50-μm-i.d. bulk fused silica capillary tubing of length 0.15–0.51 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 constant flow rate. The capillary extends 5 cm into a preheated section consisting of 0.635-cm-i.d. copper tubing 0.6 m long wrapped by heating tape, where the liquid is completely vaporized. The vapor then flows through the dew point sensor, which is maintained 5 K higher than the dew point temperature by a Blue M Stabil-Therm gravity convection oven (model OV12A), stable to ±0.2 K. When the vapor flows through the dew point sensor (General Eastern Model 2), the platinum mirror inside the sensor is thermoelectrically cooled. The temperature control of the mirror is done by the General Eastern Hygro M-3 electronic unit. 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 cools, dew forms on the mirror surface, scattering the light emitted by the diode and reducing the reflected intensity. The mirror temperature is maintained at the dew point of the sample, allowing a constant layer of dew on the mirror. The vapor exits the oven and is then condensed and collected in an ice trap. The entire system is maintained at constant pressure by an MKS high-accuracy Baratron system, capable of resolution to 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 cm³/min. 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

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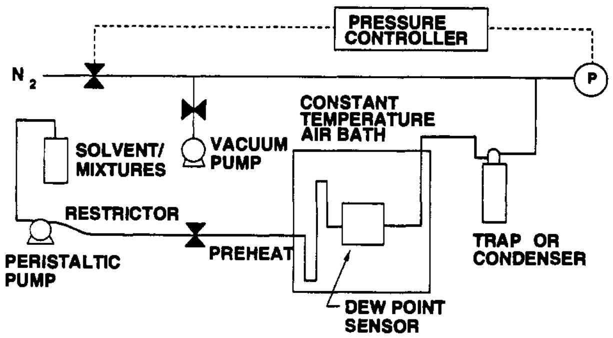

Figure 1. Overall design of the system used to measure limiting activity coefficients by dew point measurements.

Table 1. Activity Coefficients of *N,N*-Dimethylformamide (1) Infinitely Diluted in Water, γ_1^∞

T/K	γ_1^∞	T/K	γ_1^∞
292.0	0.6 ± 0.1	328.3	1.0 ± 0.1
308.3	0.7 ± 0.1	337.8	1.1 ± 0.1
318.1	0.8 ± 0.1	347.4	1.1 ± 0.1

system pressure are collected with a data acquisition system in a personal computer. The γ^∞ value at each temperature was measured at least twice, and error estimates are based on measurement uncertainties and on the replicate data. Details of the method are given elsewhere (*10*).

Chemicals

The water used in this experiment was Aldrich HPLC grade purity. The solutes were also obtained from Aldrich with a stated purity of >98%, and verified with gas chromatography. The water content of the pure solutes was determined with a Mitsubishi Kasei Karl-Fisher device and found to be negligible. Solutions of the diols in water were constructed gravimetrically with compositions ranging from 0.01 to 0.1 mol %. Although some solutes have optically active sites, only the racemic mixtures were studied in this investigation.

Results

Values of γ^∞ for *N,N*-dimethylformamide (DMF) infinitely diluted in water were measured at 298–348 K as a check (Table 1), and are in agreement with data from other sources (*10, 18–22*) (Figure 2). Differential ebulliometry is of limited precision for low relative volatility systems such as this ($\alpha = 0.1$ at 298 K), and γ^∞ from extrapolated VLE data are even more in doubt. There is some disagreement with the dew point data (*10*) at the higher temperatures which is where this technique is less accurate; however, it is within the experimental uncertainty.

The experimental data for the seven diols studied are listed in Table 2, and shown in Figure 3. For four of these diols, some vapor–liquid equilibrium (VLE) data exist, and the measured values of this work are compared with γ^∞ values extrapolated from classical VLE measurements in Figures 4 (ethylene glycol) (*23–31*), 5 (1,2-propanediol) (*24, 32, 33*), 6 (1,4-butanediol) (*33, 34*), and 7 (2,3-butanediol) (*35–37*). The saturation (vapor) pressures for the solutes and water were obtained from Gmehling et al. (*38, 39*), who fitted VLE data to provide vapor pressure relations, and Daubert and Danner's tables (*40*). For the system 1,2-butanediol it was necessary to extrapolate the vapor pressure expression outside its working range, since no other vapor pressure data were available. In the future, if such experimental data become available, the results should be reevaluated.

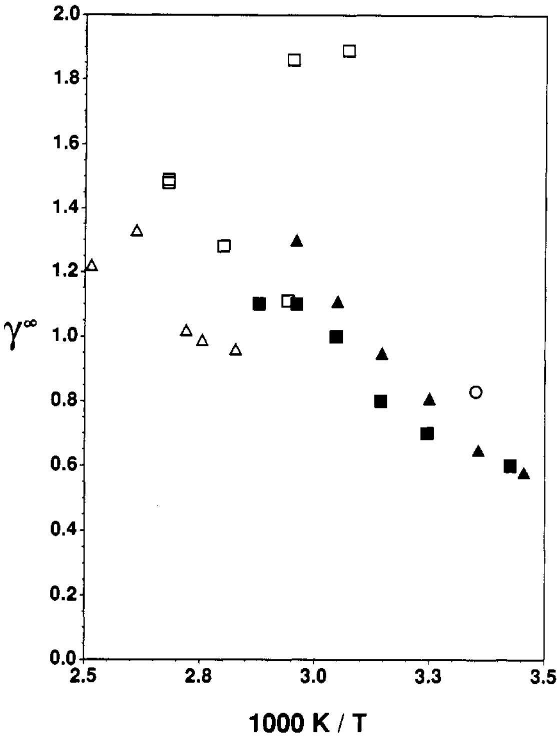

Figure 2. Comparison of γ^∞ values for DMF in water measured by the dew point method with values obtained by other sources: (■) this investigation, (□) VLE extrapolated (*18–20*), (▲) dew point experiment (*10*), (△) ebulliometric (*21*), (○) headspace chromatography (*22*).

Table 2. Activity Coefficients of Diols (1) Infinitely Diluted in Water, γ_1^∞

solute	T/K	γ_1^∞	solute	T/K	γ_1^∞
1,2-ethanediol	297.5	0.8 ± 0.1	1,3-butanediol	299.1	2.2 ± 0.2
	308.2	0.8 ± 0.1		308.8	2.3 ± 0.2
	317.9	1.0 ± 0.1		318.3	2.4 ± 0.3
	328.2	1.0 ± 0.1		327.3	2.4 ± 0.3
	338.1	1.0 ± 0.1		338.1	2.5 ± 0.3
	348.1	1.2 ± 0.2		348.0	2.6 ± 0.3
1,2-propanediol	296.8	1.0 ± 0.1	1,4-butanediol	299.4	2.8 ± 0.3
	308.3	1.1 ± 0.1		309.1	2.8 ± 0.3
	318.8	1.2 ± 0.1		318.4	2.9 ± 0.3
	328.5	1.2 ± 0.2		326.8	3.0 ± 0.3
	337.9	1.3 ± 0.2		337.6	3.0 ± 0.3
	348.3	1.3 ± 0.2		349.9	3.1 ± 0.4
1,3-propanediol	298.0	1.2 ± 0.2	2,3-butanediol	299.0	1.6 ± 0.2
	307.9	1.2 ± 0.2		308.9	1.7 ± 0.2
	318.7	1.7 ± 0.2		318.5	1.9 ± 0.2
	328.7	1.8 ± 0.2		327.4	2.1 ± 0.2
	338.4	1.9 ± 0.2		337.7	2.2 ± 0.3
	347.5	1.9 ± 0.2		347.4	2.4 ± 0.3
1,2-butanediol	299.2	2.0 ± 0.2			
	308.4	2.1 ± 0.2			
	318.1	2.2 ± 0.2			
	327.3	2.3 ± 0.3			
	338.6	2.4 ± 0.3			
	348.4	2.4 ± 0.3			

The values of γ^∞ for ethylene glycol show slight negative deviations from Raoult's law at the lower temperatures and modest positive deviations at the highest temperature. These data are consistent with a picture of both solvation of the glycol by water as well as possibly some association of the glycol. At the lower temperatures the unlike interactions are sufficiently strong to give net negative deviations, outweighing both the association and the nonspecific forces, both of which result in positive deviations.

The propanediols go from nearly ideal at the lower temperatures to exhibiting larger positive deviations at the

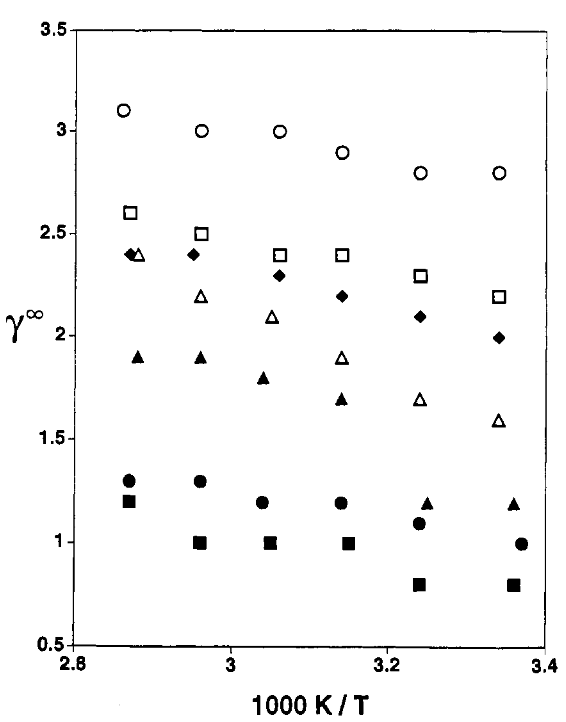

Figure 3. Comparison of γ^∞ values for various diols in water measured by the dew point method: (■) 1,2-ethanediol, (●) 1,2-propanediol, (▲) 1,3-propanediol, (♦) 1,2-butanediol, (□) 1,3-butanediol, (○) 1,4-butanediol, (△) 2,3-butanediol.

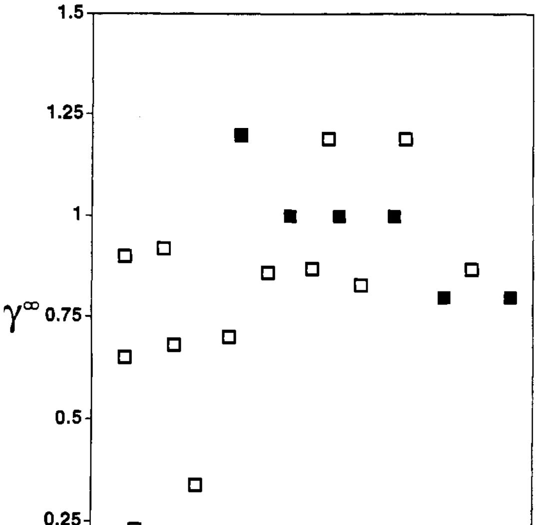

Figure 4. Comparison of γ^∞ values for 1,2-ethanediol in water measured by the dew point method with values obtained by other VLE extrapolated sources: (■) this investigation, (□) VLE extrapolated *(23–31)*.

higher temperatures. The butanediols exhibit moderate positive deviations at the lowest temperatures, which become more pronounced with increasing temperature. These data are consistent with the same molecular picture as that for the ethylene glycol.

The results for the C_3 and C_4 diols also demonstrate the effect of intramolecular hydrogen bonding: The deviations from Raoult's law become more positive as the separation of the OH moieties increases along the hydrocarbon chain.

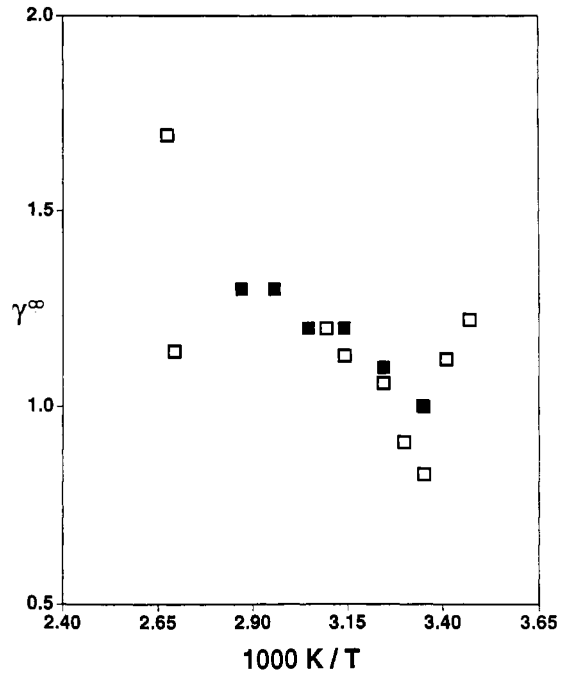

Figure 5. Comparison of γ^∞ values for 1,2-propanediol in water measured by the dew point method with values obtained by other VLE extrapolated sources: (■) this investigation, (□) VLE extrapolated *(24, 32, 33)*.

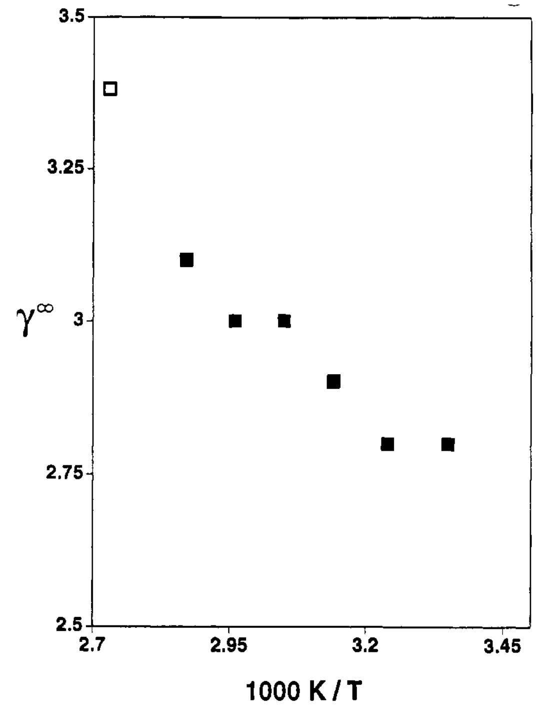

Figure 6. Comparison of γ^∞ values for 1,4-butanediol in water measured by the dew point method with values obtained by other VLE extrapolated sources: (■) this investigation, (□) VLE extrapolated *(33–34)*.

Such results cannot be explained in terms of increased solvation due to the breaking of intramolecular hydrogen bonds, nor in terms of decreased water association. Rather we suggest that this effect may be due to diol–diol association, which is facilitated by the inability of the OH moieties to engage in intramolecular hydrogen bonding.

The differences in γ^∞ can be followed with those of vapor pressures. The trend of increasing γ^∞ from 2,3-butanediol to 1,2-butanediol to 1,3-butanediol and to 1,4-butanediol agrees with that of decreasing vapor pressures, or simply increasing boiling points: 455.7, 463.7, 480.7, and 508.2

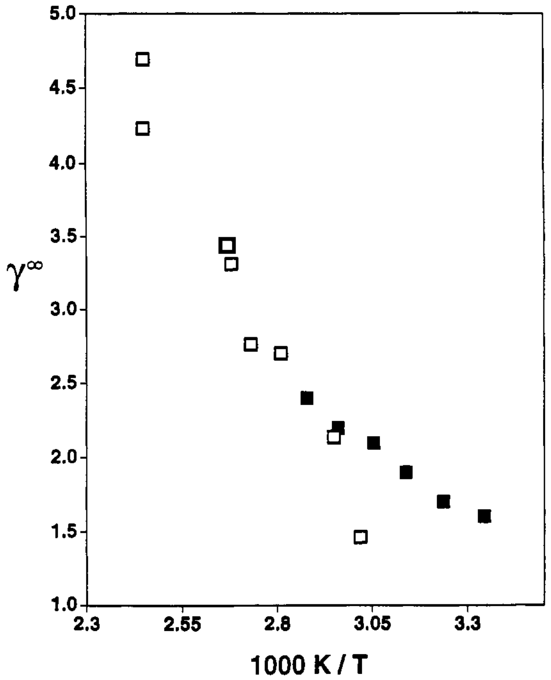

Figure 7. Comparison of γ^∞ values for 2,3-butanediol in water measured by the dew point method with values obtained by other VLE extrapolated sources: (■) this investigation, (□) VLE extrapolated (*35–37*).

Table 3. Estimated γ_2^∞ Values of Water in Various Diols at 298 K Calculated from Experimental γ_1^∞ Values of Diols in Water Using a One-Parameter Wilson Equation (λ_{22} = 8.30 kJ·mol^{-1})

solvent	λ_{11}/(kJ·mol^{-1})	λ_{12}/(kJ·mol^{-1})	estimated γ_2^∞ of water
1,2-ethanediol	11.25	9.71	0.8 ± 0.2
1,2-propanediol	10.86	9.99	0.9 ± 0.2
1,3-propanediol	11.04	10.19	1.0 ± 0.2
1,2-butanediol	11.02	10.80	1.2 ± 0.2
1,3-butanediol	11.12	10.92	1.3 ± 0.2
1,4-butanediol	12.84	11.87	1.7 ± 0.2
2,3-butanediol	10.98	10.59	1.1 ± 0.2

K, respectively. This also suggests that intermolecular diol–diol hydrogen bonding increases as the separation of the OH's decreases the intramolecular hydrogen bonding.

Modeling with Wilson's Equation

Since this investigation studied only one end of the binary system, a one-parameter Wilson equation (*41*) was used to model the experimental results. The one-parameter Wilson equation consists of using λ_{12} as the only adjustable parameter instead of using the two differences $\lambda_{12} - \lambda_{11}$ and $\lambda_{12} - \lambda_{22}$. The like-pair potentials, λ_{ii}, were estimated from the configurational energy following the procedure of Wong and Eckert (*42*). Naturally this method fits the data well at one end of the composition range, but it was also used to predict γ^∞ for the other composition extreme, water infinitely diluted in the diol. The results along with the parameters are shown in Table 3. The results show that although such extrapolations are highly speculative in strongly hydrogen-bonded systems, for these systems (except perhaps for 1,4-butanediol), the predictions were surprisingly in accord with the various extrapolations available from VLE data (Figure 8).

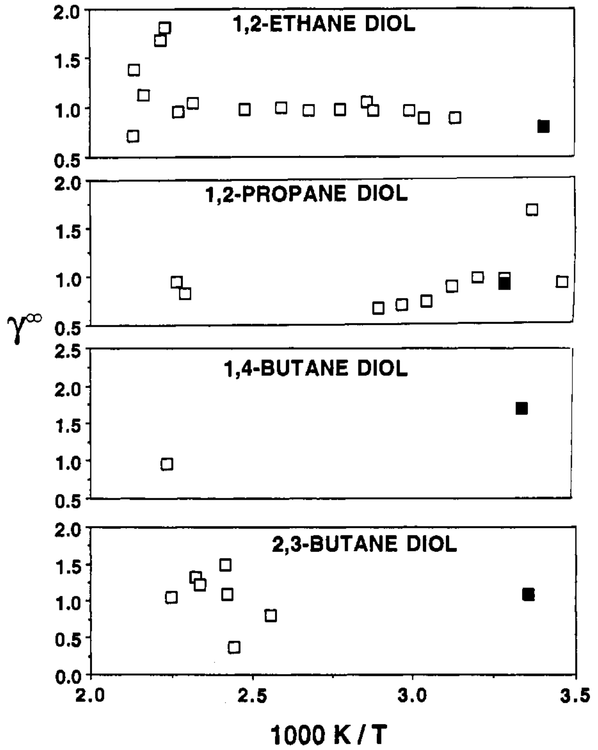

Figure 8. Comparison of γ^∞ values for water in various diols: (■) prediction from dew point γ^∞ results of the diols in water, (□) values obtained by other VLE extrapolated sources (*23–37*).

Table 4. Experimental Partial Molar Excess Enthalpy at Infinite Dilution, $\bar{h}_1^{E,\infty}$ of Various Diols in Water Calculated from Experimental γ_1^∞ in Water

solute	$\bar{h}_1^{E,\infty}$/ (kJ·mol^{-1})	solute	$\bar{h}_1^{E,\infty}$/ (kJ·mol^{-1})
1,2-ethanediol	−7 ± 4	1,3-butanediol	−3 ± 2
1,2-propanediol	−4 ± 3	1,4-butanediol	−2 ± 2
1,3-propanediol	−8 ± 4	2,3-butanediol	−8 ± 5
1,2-butanediol	−3 ± 2		

Partial Molar Enthalpy at Infinite Dilution

The slope of the γ^∞ data versus temperature yields the partial molar excess enthalpy at infinite dilution, $\bar{h}_i^{E,\infty}$ (*43*). Among the systems studied, the 1,3-propanediol γ^∞ shows the largest curvature versus (1/*T*); however, this variation is small and within the experimental error. However, because of strong hydrogen bonding, these systems are not regular, and any linearity must be viewed as fortuitous.

Because of the limited temperature range, the data were fit linearly to yield values of $\bar{h}_i^{E,\infty}$ (Table 4). There is considerable uncertainty in these results, and it is always preferable to measure this quantity directly with a technique such as asymmetric isothermal flow calorimetry (*44*).

Summary

Limiting activity coefficients for various diols in aqueous solutions were measured using a dew point technique, designed for low relative volatility systems. The results are discussed in terms of the relative intramolecular and intermolecular hydrogen bonding. A one-parameter Wilson equation was fit to the results, and used to estimate γ^∞ for water in the diols. Partial molar excess enthalpies at infinite dilution were calculated from the temperature derivative of the limiting activity coefficients.

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Notation

γ_i^∞	activity coefficient at infinite dilution
$\bar{h}_i^{E,\infty}$	partial molar enthalpy at infinite dilution
ϕ_i	fugacity coefficient of the vapor
ϕ_i^s	fugacity coefficient at the saturation pressure
λ_{ii}	characteristic energy of the Wilson equation
P	total pressure
P_i^s	saturation pressure
R	gas constant
T	temperature
v_i	liquid molar volume
x_i	composition

Subscripts

1	solvent
2	solute

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