tabulated in Table 12. As seen from this table, the comparison of the azeotropic composition and azeotropic total vapor pressure between this work and the calculated literature values agrees well with the difference less than 0.02 mole fraction and 1.5 mm Hg, respectively.

Nomenclature

a, b, c = Antoine constants
C_1, C_2, C_3, C_4 = constants
B, C, D = Redlich-Kister parameters
G^E = Molal excess Gibbs free energy
P = total vapor pressure
p = vapor pressure of pure component
R = gas constant
T = temperature, K
t = temperature, °C
V = liquid molal volume of pure component
x = mole fraction in liquid phase
y = mole fraction in vapor phase
$\beta_{11}\beta_{22}$ = second virial coefficient of pure components 1 and 2, respectively
β_{12} = cross second virial coefficient
γ = activity coefficient
δ = defined by Equation 3

Subscripts

$1, 2, i, j$ = components
calc = calculated value

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Densities and Partial Molal Volumes of Water-Ethylene Glycol Mixtures

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Densities and partial molal volumes of water-ethylene glycol mixtures were determined at 25° and 38.5°C. The densities can be expressed in terms of fourth-degree polynomials with respect to the mole fraction of ethylene glycol. The partial molal volume of ethylene glycol had a minimum at both temperatures, occurring at the respective mole fractions 0.063 and 0.053. In the mole fraction range 0.64-0.74 ethylene glycol, the partial molal volumes were nearly constant. This might be due to the presence of hydrogen-bonded aggregates in the mixture.

In connection with a study of micelle formation in water-ethylene glycol mixtures (*7*), we determined the densities and partial molal volumes of the two-component solvent mixtures at two temperatures. These data were of interest in comparisons of the behavior of ethylene glycol and of monohydric alcohols in aqueous mixtures (*8*). Deviations from ideality in ethanol-water mixtures were related to alcohol-water interactions and to changes in liquid structure (*1*). Densities and partial molal volumes of water-ethylene glycol mixtures were determined at 25°C by Timasheff and Inoue (*9*) and at 20°C by Nakanishi (*4*), but few data points were taken at high glycol concentrations ($x_2 > 0.9$). No comparative measurements at higher temperatures are available.

Experimental

Fisher "certified" ethylene glycol was dried overnight with anhydrous Na_2SO_4, distilled in vacuum (5-mm Hg pressure, 60-65°C), and stored under dry nitrogen.

Measurements were made with a 10-ml Sprengel-type pycnometer, calibrated with distilled water at the temperatures of the measurements. Prior to weighings, it was thermostated by immersion in the main bath of a Haake model "NBe" constant-temperature circulator, regulated to within ±0.05°C. The weighings were corrected for air buoyancy.

Results

The density can be expressed as a polynomial in x_2, the mole fraction of ethylene glycol. With a least-squares fitting technique, fourth-degree polynomials gave best

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fits to the experimental data, as judged by the Gauss statistical criterion (*10*).

$$\rho(25^\circ) = 0.99722 + 0.42114\,x_2 - 0.72022\,x_2^2 + 0.62036\,x_2^3 - 0.20911\,x_2^4 \quad (1)$$

$$\rho(38.5^\circ) = 0.99306 + 0.3996\,x_2 - 0.7058\,x_2^2 + 0.6450\,x_2^3 - 0.2309\,x_2^4 \quad (2)$$

The values of the Gauss criterion were 0.559×10^{-6} at 25°C (for 25 data points) and 0.163×10^{-6} at 38.5°C (for 20 data points). The values were at least fifteenfold higher for third- or fifth-degree polynomials.

Partial molal volumes were calculated from Equation 3 for ethylene glycol ($\bar{V}_2$) and the corresponding equation for water ($\bar{V}_1$),

$$\bar{V}_2 = \frac{M_2}{\rho} - \frac{M_1 + x_2(M_2 - M_1)}{\rho^2}\frac{\partial \rho}{\partial x_2}(1 - x_2) \quad (3)$$

where M_1 and M_2 are the molecular weights of water and of ethylene glycol, respectively (based on derivations in Ref. *2*).

The results are shown in Figure 1, represented as the "excess partial molal volume of mixing," $\bar{V}_i - V_i°$ (with i = 1 or 2), where the $V_i°$ are the molal volumes of the pure components. Numerical values of $V_i°$ were taken from the computed smooth curves of $\bar{V}_i$ vs. x_2: $V_1° = 18.066$ and 18.142 cm³/mol for water, and $V_2° = 55.949$ and 56.378 cm³/mol for ethylene glycol at 25° and 38.5°C, respectively.

Calculations were carried out on the PDP-15 computer of the Rockefeller University Computer Center.

Discussion

Our results agree well with the earlier determinations (*4, 9*) near room temperature. The minimum in $\bar{V}_2$ was reported to occur near 15 vol % ($x_2 = 0.055$) at 25°C (*9*) and at $x_2 = 0.06$ at 20°C (*4*). We found it at $x_2 = 0.063$ at 25°C and at $x_2 = 0.053$ at 38.5°C with a depth $\bar{V}_2 - V_2° = -1.467$ and -1.272 cm³/mol, respectively. The values reported in the literature are -1.46 cm³/mol at 25°C (*9*) and -1.68 cm³/mol at 20°C (*4*). The position of the minimum is affected only slightly by temperature changes, but the depth decreases with a rise in temperature. Thus, the reported value at 20°C is qualitatively consistent with our data at higher temperatures.

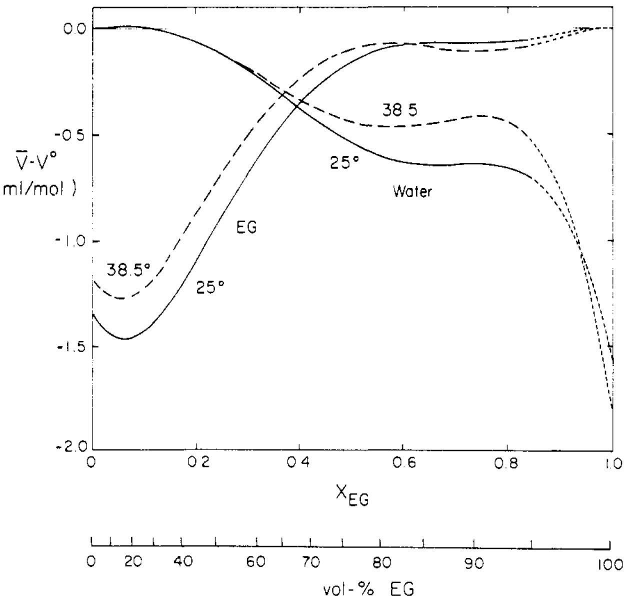

Figure 1. Partial molal volumes of water and ethylene glycol in binary mixtures at 25° (full lines) and at 38.5°C (dashed lines)

Dotted portions indicate where curves are sensitive to details of numerical analysis

The temperature dependence of $\bar{V}_2$ at low alcohol concentrations parallels that for ethanol (*1*). However, as pointed out by Nakanishi et al. (*5*), the relative depth of the minimum is much lower for diols than for the monohydric alcohols. Although no definite conclusions can be drawn about the structure of the mixed liquids from the density data alone, the similarity in behavior suggests that structural effects similar to those postulated for monohydric alcohols (*1*) occur in water-ethylene glycol mixtures as well, and that they persist over a limited temperature range. Discontinuities in the association behavior of lactoglobulin A at acid pH have been observed in the same concentration range (*3*); it was suggested (*3*) that they might be due to changes in the structure of the solvent.

The rapid decrease in $\bar{V}_1$ as x_2 approaches unity is similar to the behavior in water-ethanol mixtures (*1*), although the value of $\bar{V}_1 - V_1°$ is smaller for ethylene glycol, like the relative magnitude of $\bar{V}_2 - V_2°$ in the region of low x_2. Although the changes in the structure of the mixed solvent and/or the packing of the two kinds of molecules (caused by alteration of the composition) are similar in kind, apparently, they are quantitatively much smaller in water-ethylene glycol mixtures.

An unusual feature is the nearly constant value of $\bar{V}_i$ in the concentration range $x_2 = 0.64$–0.74. No explanation has been found for this phenomenon. We applied Equation 3 to the density data reported by Nakanishi et al. (*5*) for several propanediols and butanediols. A nearly horizontal stretch of the $\bar{V}_1$ curve or even a slight maximum (similar to that seen on the 38.5°C curve near $x_2 = 0.75$ in Figure 1) appears in the same approximate concentration range for all of them.

In water-ethanol mixtures, there is a region of positive curvature of the $\bar{V}_1$ curve in a similar concentration range (*1*), but the change in slope is less marked than for diols. The cause for this behavior may be similar. This concentration range is least studied for alcohol-water mixtures. Since water and ethylene glycol in mixtures may form some kinds of spatially extended structures (*6*), one might speculate that such structures undergo little if any change in the composition range mentioned. This, in turn, raises the question whether a similar form of molecular aggregation may also occur in ethanol-water mixtures. (Tentative proposals of the existence of large molecular aggregates at extremely high alcohol concentrations in water were reviewed in Ref. *1*.) The data cited here do not suffice as the basis of a secure interpretation in terms of liquid structure. More extensive studies of various properties in this concentration range would be desirable.

A warning is sounded with regard to computational analysis and numerical fitting of data such as those presented here. Computed curves of partial molal volumes are sensitive in the high x_2 region to the degree of the polynomial used to fit the density data (Equations 1 and 2), and the appearance of the curves may change strongly in this range. Therefore, it is imperative that the form of the equation representing the density data be checked, not only by computing the statistical criteria of goodness of fit, but by estimating partial molal volumes with an independent method not linked to the functional form of Equation 1, such as by graphical analysis. In the present case, such an analysis confirmed the correctness of the fourth-degree polynomial.

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Phase-Equilibria Behavior of Systems Carbon Dioxide-*n*-Eicosane and Carbon Dioxide-*n*-Decane-*n*-Eicosane

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The phase-equilibria behavior of the binary mixture CO_2–*n*-eicosane was studied for vapor-liquid, solid-liquid-vapor, and liquid-liquid-vapor systems. The ternary mixture CO_2–*n*-decane–*n*-eicosane was studied for the liquid-liquid-vapor system in the temperature range of 29–33°C, and CO_2-free selectivities between the liquid phases are presented. Liquid CO_2 demonstrated a marked tendency toward selectivity which suggests possible separational design applications.

Phase-equilibria studies of CO_2–paraffin mixtures have been conducted by a large number of investigators, involving paraffins ranging from methane to hexadecane. Partial miscibility has been observed in mixtures of the heavier paraffins with CO_2 and suggests the use of CO_2 as an extractive agent, its success being dependent upon the selectivity of CO_2 with respect to different hydrocarbons between liquid phases.

The purpose of this paper is to present data on the binary system CO_2–*n*-eicosane and the ternary system CO_2–*n*-decane–*n*-eicosane which we feel support the proposed use of CO_2 as an extractive agent. The initial choice of a paraffinic mixture in the ternary system was based on the desire to understand better the phase behavior of CO_2–paraffin systems; our long-range plan is to study diverse hydrocarbon mixtures, e.g., aromatic–paraffinic, with CO_2 to establish broad selectivity criteria which would aid in separational process design for petroleum fractions in general.

The citation of previous phase-equilibria studies of CO_2–paraffin systems will be restricted to those exhibiting partial miscibility phenomena. Reamer and Sage (*7*) extensively studied the CO_2–*n*-decane binary system, obtaining P-V-T-x data for vapor-liquid equilibria up to 460°F. Stewart and Neilsen (*9*) reported solubility data at 60° and 90°F for binary systems of CO_2 with *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane, including partial miscibility data for the last two systems. Schneider (*8*) obtained P-T-x binary-phase equilibrium data for CO_2 in *n*-octane, *n*-undecane, *n*-tridecane, and *n*-hexadecane in the temperature range $-120°$ to 400°C at pressures up to 3700 atm. Partial miscibility phenomena were observed in all systems studied.

Ternary studies were conducted by Meldrum and Nielsen (*6*) who investigated the liquid-liquid-vapor region of the systems involving CO_2 with the paraffin pairs propane–*n*-hexadecane and *n*-decane–*n*-hexadecane. Gupta (*2*) studied the coexistence region for the ternary systems CO_2 with *n*-hexane–*n*-hexadecane, *n*-decane–*n*-hexadecane, and *n*-dodecane–*n*-hexadecane. A general treatise on the immiscibility of CO_2 in 461 ternary systems was presented by Francis (*1*), in which different types of immiscibility behavior are categorized.

Our choice of *n*-decane as one of our paraffinic components was governed by the availability of the excellent volumetric data of Reamer and Sage (*7*). Similar treatment of the system CO_2–eicosane was deemed necessary by us since volumetric data are not only useful for design purposes but also are needed to apply correlative solution models. Our binary study involves the experimental determination of the vapor-liquid, liquid-liquid-vapor, and solid-liquid vapor equilibrium of the CO_2–*n*-eicosane system. We are unaware of any systematic treatment of the system CO_2–*n*-eicosane. P-T-V-x data are taken for the phases in equilibrium, and critical points such as the type-K singular point, as well as the Q point for this system, were determined. It is hoped that a detailed study of the CO_2–*n*-eicosane system, in combination with the previously cited CO_2–*n*-decane study, would lend additional insight into the behavior of CO_2 mixtures with intermediate normal paraffins, for which only solubility data presently exist.

The primary focus of the ternary study is on liquid-liquid-vapor systems, specifically the selectivity of the liquid phases. Hydrocarbon selectivities were determined from samples on a CO_2-free basis.

Experimental Apparatus

The apparatus used in this study is the same as that used in earlier studies (*3–5*). Briefly, a P-V-T apparatus was used in conjunction with a viewable 10-cm^3 glass equilibrium cell. Temperature was measured with a Pt-resistance thermometer to ±0.05°C. Pressure was measured with Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge, to ±0.07 atm. The viewable glass cell was carefully calibrated and judged to be accurate to ±0.02 cm^3. This configuration was used for all binary runs and also the ternary "scanning" runs, the latter being used to provide information on the thermodynamic location of the L1-L2-

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