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Physical Properties (Density, Excess Molar Volume, Viscosity, Surface Tension, and Refractive Index) of Ethanol + Glycerol

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The physical property data (densities, excess molar volumes, viscosities, surface tensions, and refractive indices) for ethanol + glycerol have been determined at 294 K and atmospheric pressure. Densities were determined by a vibrating-tube densitometer, viscosities were determined by U-tube viscometers, surface tensions were determined by the Du Noüy ring method, and refractive indices were determined by an Abbe refractometer. Excess molar volumes were computed from density values and were fit to the Redlich−Kister equation.

Introduction

Both ethanol and glycerol are important solvents in the pharmaceutical and food industries. They are completely miscible. However, no experimental density, viscosity, and surface tension data for mixtures of these compounds have been presented in literature. They can also be used as convenient fluid analogues for laboratory investigations of mixing between heavy oil and hydrocarbon gas or carbon dioxide relevant to the vapor extraction (VAPEX) oil recovery process. In this process, a low-viscosity solvent is injected into a deposit of heavy oil. This solvent mixes with the oil, reduces its viscosity, and improves the rate at which it is produced. Early experiments showed that the mass transfer mechanisms between oil and solvent are poorly understood.[1−6] In the planning of further experiments for investigating the mechanisms and rates of mass transfer between oil and solvent, ethanol and glycerol have been selected to represent injected solvent and oil, respectively. Analysis of diffusion and dispersion in a porous medium is considerably more simple if a binary, first-contact miscible fluid system is used rather than multicomponent hydrocarbons whose composition and phase behavior are generally poorly characterized.[7,8]

In this work, the densities, excess molar volumes, viscosities, surface tensions, and refractive indices of ethanol + glycerol are presented at 294 K and ambient pressure over the whole range of compositions. All data are also presented as correlations in the mole fraction of ethanol to allow indirect determination of the composition of arbitrary mixtures.

Experimental Section

Materials. Both ethanol and glycerol were provided by VWR International with stated purities of 99.99 % and 99.75 %, respectively, and were used as provided without further purification. The purities of the fluids were sufficient for the determination of the system's physical property behaviors at ambient pressure and temperature described in this work. In addition, we checked the purities of the fluids used by determining their properties such as densities and refractive indices, which were in very good agreement with values found in the literature, as shown in Table 1.

Table 1. Properties of Pure Components at 294 K and Comparison with Literature Values

	ρ / kg·m^{-3}		η / mPa·s		σ / mN·m^{-1}		n_D	
component	exptl	lit.	exptl	lit.	exptl	lit.	exptl	lit.
ethanol	789.91	789.90[9]	1.214	1.200[11]	22.2	22.2[13]	1.3618	1.3616[13]
glycerol	1261.51	1261.30[10]	1390	1412[12]	63.1	63.3[14]	1.4740	1.4740[10]

Table 2. Densities (ρ), Viscosities (η), Surface Tensions (σ), Excess Molar Volumes (V_m^E), and Refractive Indices (n_D) of Ethanol (1) + Glycerol (2) at 294 K and Atmospheric Pressure

x_1	ρ / kg·m^{-3}	η / mPa·s	σ / mN·m^{-1}	V_m^E / cm^3·mol^{-1}	n_D
0.0000	1261.51	1390	63.1	0	1.4740
0.0840	1233.48	800.5	52.0	− 0.245	1.4680
0.1222	1220.30	627.9	48.8	− 0.351	1.4660
0.1761	1201.19	450.0	43.0	− 0.500	1.4619
0.2037	1191.35	385.1	41.7	− 0.584	1.4592
0.2385	1178.37	270.0	39.4	− 0.666	1.4562
0.2789	1162.98	220.5	35.8	− 0.761	1.4528
0.3510	1134.30	141.4	33.2	− 0.908	1.4470
0.4138	1108.32	80.71	29.7	− 1.024	1.4392
0.4841	1077.53	54.01	28.5	− 1.114	1.4326
0.5497	1047.03	31.52	27.1	− 1.146	1.4253
0.6046	1020.27	20.31	25.1	− 1.143	1.4179
0.6526	995.96	16.70	24.3	− 1.120	1.4131
0.7451	946.41	9.096	23.5	− 0.995	1.4016
0.7984	916.05	5.217	23.5	− 0.869	1.3934
0.8336	895.63	4.100	23.0	− 0.781	1.3885
0.8777	868.79	3.037	22.5	− 0.615	1.3815
0.9353	832.89	1.898	22.4	− 0.387	1.3727
0.9596	816.85	1.490	22.3	− 0.244	1.3681
1.0000	789.91	1.214	22.2	0	1.3618

Methods. The physical properties of 20 different ethanol + glycerol mixtures were investigated. The mixtures were prepared by mass by the use of a Mettler PM460 DeltaRange balance with an uncertainty of ± 0.001 g. The estimated mole fraction uncertainty was less than $\pm 10^{-3}$. All measurements were made at atmospheric pressure and 294.0 K. The temperature was kept constant through the use of a water bath with an uncertainty of ± 0.1 K.

Density Measurements. The density of each mixture was measured with an Anton Paar DMA60/602 density meter to an

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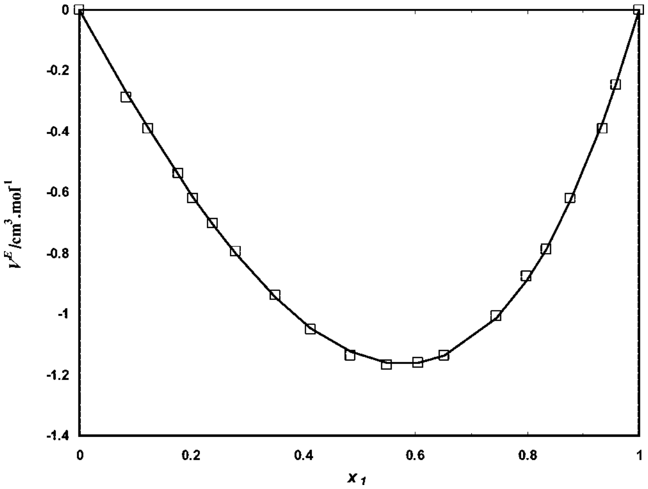

Figure 1. Excess molar volumes (V_m^E) for ethanol (1) + glycerol (2) at 294 K and atmospheric pressure: □, experiment points; —, Redlich–Kister fitted curve (eq 2).

Table 3. Coefficients of Equation *2* and the Standard Deviation $\sigma(V_m^E)$

cm^3·mol^{-1}				
A_0	A_1	A_2	A_3	$\sigma(V_m^E)$
− 4.4656	1.4642	− 0.1230	0.3820	0.0075

Table 4. Calibration of Viscometers at 294 K

tube no.	constant, c mm^2·s^{-2}	range of μ mm^2·s^{-1}	calibration fluid(s)
25	0.002	0.5 to 2	water, oil
50	0.004	0.8 to 4	water, oil
100	0.015	3 to 15	oil
150	0.035	7 to 35	oil
200	0.100	20 to 100	0.85[a]
300	0.250	50 to 250	0.85[a]
350	0.500	100 to 500	0.95[a]
400	1.200	240 to 1200	0.97[a]
450	2.500	500 to 2500	0.98[a]

[a] Values of glycerol mass fraction from ref 12.

uncertainty of ± 0.01 kg·m^{-3}. A refrigerated bath (Techne RB-12) was used to circulate water and to keep the temperature constant. The estimated uncertainty in the density measurement including possible variations in temperature of ± 0.1 K is ± 0.1 %.

The density meter was calibrated with water and dry air as per the manufacturer's instructions (DMA instruction manual; Anton Paar, Graz, Austria). After each measurement, the U-tube cell was cleaned with 5 mL of ethanol. Then, dry air was passed through the cell to evaporate any remaining liquid. This process continued until the oscillation period was that of the dry air obtained in the initial calibration. Each measurement was repeated at least twice to check reproducibility.

The excess molar volumes were calculated from the density data as

$$V_m^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (1)$$

where M_i is the molar mass of component i, ρ and ρ_i are the densities of the mixture and component i, respectively, and x_i is the mole fraction of component i.

The computed excess molar volumes V_m^E for the 20 mixtures of ethanol + glycerol are listed in Table 2 and are graphically presented in Figure 1. The V_m^E values were correlated with the Redlich–Kister polynomial[15]

$$V_m^E/(\text{cm}^3\text{·mol}^{-1}) = x_1x_2\sum_{i=0}^{m} A_i(x_1 - x_2)^i \qquad (2)$$

where A_i is a fitting parameter whose value was obtained by the least-squares method using Polymath 5.1 (Polymath Software, Willimantic, CT) and m is the degree of the polynomial expansion. The coefficient A_i and the corresponding standard deviations obtained are given in Table 3. The standard deviation was calculated using the following expression

$$\sigma(V_m^E) = \left(\frac{\sum_i^{N_D} (V_{\text{exptl}} - V_{\text{corr}})^2}{N_D - N_P} \right)^{1/2} \qquad (3)$$

In this equation, V_{exptl} and V_{corr} are the experimental and correlated V_m^E values, respectively, N_D is the number of data points, and N_P is the number of parameters. As can be seen in Figure 1, the excess molar volumes correlate well with the Redlich–Kister polynomial expansion.

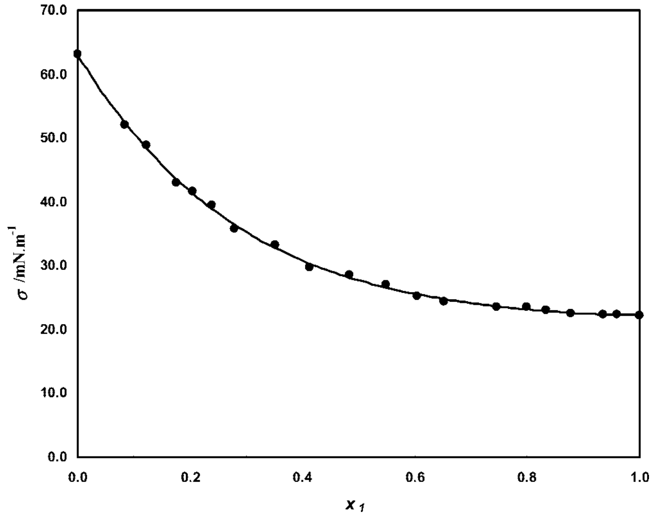

Figure 2. Surface tension (ν) for ethanol (1) + glycerol (2) at 294 K and atmospheric pressure: ●, experiment points; —, eq 6.

Viscosity Measurements. The viscosity of each sample was measured using a U-tube (Cannon-Ubbelohde) viscometer immersed in a water bath at a temperature of 294 K, which was kept constant by the use of a refrigerator (Townson and Mercer). In total, nine different viscometers of different capillary sizes were used to cover the whole range of mixture viscosities. Each U-tube has a characteristic constant (c) associated with the size of its capillary. The time (t) required for fluid to flow through the capillary between two predetermined lines was measured by the use of a digital stop clock (TM 20) to an uncertainty of 0.01 s. The kinematic viscosity (μ) was calculated from

$$\mu = c \cdot t \qquad (4)$$

The viscometers were filled with 15 mL of test sample for each measurement. For viscometers with small capillary sizes (tubes nos. 25 and 50), the standard fluid viscosity was water with values taken from standard tables, and the density was determined by a densitometer, as previously described. For larger capillary sizes, however, glycerol + water mixtures were used instead, with values taken from Segur and Oberstar,[12] which details the calibration and measurement processes. This was necessary because water would flow too quickly through these tubes and thus increase the uncertainty. In all measurements, we kept the flow times at > 200 s by selecting viscometers with appropriate values of *c*. Details of viscometers and calibration fluids used are given in Table 4. The calibration of tubes 25, 50, 100, and 150 was further confirmed with the use of the Cannon certified viscosity standard mineral oil with a density of 862.8 $\text{kg}\cdot\text{m}^{-3}$. On average, its measured viscosity of 9.397 mPa·s agrees reasonably well with the stated viscosity of 9.315 mPa·s at 294 K.

We calculated the dynamic viscosity η of each sample by multiplying its kinematic viscosity by the density. The viscosity of each sample was measured with at least two viscometers of different sizes and was repeated at least three times. The estimated uncertainty was within ± 1 %.

Values of measured viscosities are reported in Table 2. The best fit of viscosity data at a temperature of 294 K is a polynomial of the form

$$\log(\eta/\text{mPa}\cdot\text{s}) = -0.268\cdot x_1^2 - 2.811\cdot x_1 + 3.145 \qquad (5)$$

Equation 5 has an average deviation of 2 % for the range of mixtures examined.

Surface Tension Measurements. The surface tensions (σ) of ethanol + glycerol in air were measured using the Du Noüy ring method on a Krüss K10 (Hamburg) automatic tensiometer with an uncertainty of $\pm$ 0.1 $\text{mN}\cdot\text{m}^{-1}$. The platinum ring was thoroughly cleaned and flame dried prior to each measurement. Each value reported here was an average of at least three measurements where the reproducibility of the same sample was within 0.5 %.

Measured values of surface tensions are reported in Table 2 and are graphically presented in Figure 2 with the best fit curve of the form

$$\sigma\,(\text{mN}\cdot\text{m}^{-1}) = -46.71\cdot x_1^4 - 155.10\cdot x_1^3 + 210.69\cdot x_1^2 - 143.03\cdot x_1 + 63.00 \qquad (6)$$

Equation 6 fit the data of σ in Table 2 for each concentration with an average deviation of 0.16 $\text{mN}\cdot\text{m}^{-1}$.

Refractive Indices. The refractive index (n_D) of all samples was obtained using a Bellingham and Stanley Abbe refractometer (model 60/ED) with a sodium D1 line (wavelength 589.6 nm). The refractometer was calibrated with distilled water before each use as per the instrument instructions. First, the surface of the refractometer prism was cleaned using ethanol and a lens wiper. This ensured that no stains or air bubbles were left on the prism surface. Next, several drops of distilled water were placed on the prism surface using a plastic syringe and were covered with a cap. The refractive index of the distilled water was then measured at 294 K and was set at 1.333, which agrees well with the value reported in the literature.[16,17]

All measurements were made at atmospheric pressure and 294 K. The temperature was kept constant to within ± 0.1 K by circulating water into the instrument through thermostatically controlled bath (Techne RB-12). Each measurement was repeated at least three times and then averaged with a repeatability of within 0.1 %. Values of refractive indices are given in Table 2 and are plotted in Figure 3. The Figure also shows the best fit for the data, which has the form

$$n_D = -0.0104\cdot x_1^3 - 0.0362\cdot x_1^2 - 0.0658\cdot x_1 + 1.4742 \qquad (7)$$

For all mixtures examined, eq 7 has an estimated uncertainty of 0.2 %.

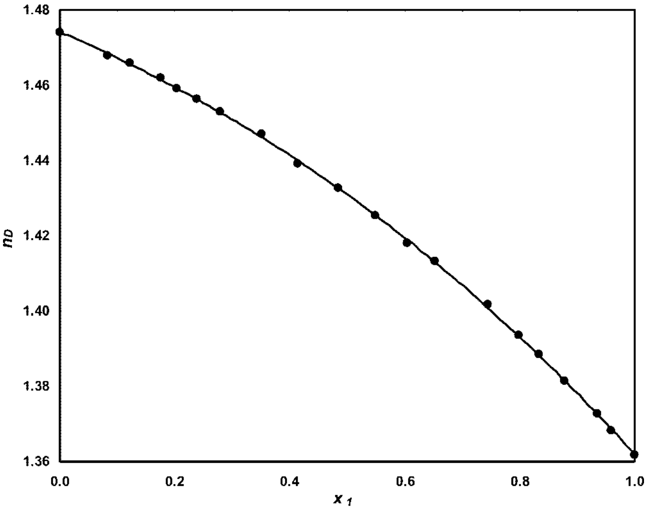

Figure 3. Refractive indices (n_D) for ethanol (1) + glycerol (2) at 294 K and atmospheric pressure: ●, experiment points; —, eq 7.

Results and Discussion

As can be seen from Table 2 and Figure 1, all values of V_m^E are negative for the entire range of mole fractions. This indicates a decrease in the overall volume of the mixture compared with simple linear additions. The contraction of the volume could be attributed to the strong hydrogen bonding that arises from the dipole−dipole interactions between the ethanol and glycerol, as found in other alcohols.[18] The results show a decrease in the magnitude of the mixture's refractive index and surface tension with an increase in ethanol concentration in the mixture.

Table 2 and Figures 1 and 2 show the effect of the addition of ethanol to glycerol on the mixture's density and viscosity. For example, a mole fraction of ethanol of 0.1 decreases the relative density of glycerol by about 3 % but more importantly decreases its viscosity by about 50 %. This reduction in viscosity resembles what happens during the VAPEX of high-viscosity crude oils in the subsurface. In practice, a low-molecular-weight solvent such as propane is injected to reduce the viscosity of heavy oil so that it can flow to the production well via gravity drainage. This process could be an important way of improving recovery from heavy oil deposits. Nonetheless, the rate of mass transfer between the solvent and crude oil in porous media is poorly understood at this time.[1−6] Ethanol and glycerol are convenient analogue fluids for the investigation of this mass transfer without the complexity of heavy oil characterization and the cumbersome lumping of its fractions.

Summary

The physical properties (viscosity, density, surface tension, and refractive index) of ethanol + glycerol have been determined at a temperature of 294 K and atmospheric pressure. Fitting parameters have been determined so that the mixture density can be described by the Redlich−Kister expansion. Simple empirical equations have also been obtained that allow the calculation of viscosity, surface tension, and refractive index from the mixture composition. In total, 20 samples were prepared that ranged from pure ethanol to pure glycerol and covered the whole composition range. The effect of increased ethanol concentration on glycerol properties is summarized in Table 2. This simple fluid system is being used to understand mass transfer during the VAPEX of high-viscosity crude oil from the subsurface better

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