Three-Phase Vapor−Liquid−Liquid Equilibria for Methane + *n*-Octane + Monoethylene Glycol + Water at Pressures from (3.1 to 15.0) MPa and Temperatures from (281 to 363) K[†]

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Experimental vapor−liquid−liquid equilibrium (VLLE) compositions have been measured, in an equilibrium cell, for the four-component system methane + *n*-octane + monoethylene glycol (MEG) + water at pressures from (3.1 to 15.0) MPa and temperatures from (281 to 363) K. A total of 27 sets of equilibrium data have been obtained using three different types of feed mixture. The relative volumes of the three phases have also been obtained for each equilibrium data set. The measurements illustrate the pressure and temperature dependence of the dehydrating effect of MEG in the vapor phase and also show that the solubility of the hydrocarbons in the aqueous phase is considerably enhanced by the presence of MEG. Some implications for the design of gas dehydration plants have been briefly discussed.

Introduction

The water present in gas streams from natural gas reservoirs may be partially separated at the well-head. The gas stream remains saturated with water at the temperature and pressure conditions of the separator. For a typical UK offshore gas field, the temperature drop which the gas stream undergoes when it is brought to the surface, and during further transmission along the sea bed, results in free (liquid) water in the pipeline. This aqueous phase may give rise to a number of problems including corrosion of steel pipelines, hydrate formation, and reduced line capacity.

There are several commercial processes available for the dehydration of gas, such as the use of liquid or solid desiccants and expansion refrigeration. The lower capital and operating costs of liquid desiccants in comparison with granular desiccants in regenerative processes have led to extensive use of various glycols for this purpose. Owing to its relatively high boiling point and decomposition temperature, triethylene glycol (TEG) has the smallest vaporization losses during the regeneration process. As discussed by Manning and Thompson,[1] TEG is commonly the most economical choice for traditional dehydration units.

On the other hand, monoethylene glycol (MEG) has the lowest viscosity of the glycols and is less soluble in hydrocarbon condensate than its higher derivatives. Therefore, MEG is usually the preferred option for glycol injection systems where glycol flows with the gas to absorb water, preventing the conditions under which hydrocarbon hydrates can form. This arrangement is particularly suited to offshore fields where the glycol regeneration plant can be sited onshore, and the glycol returned to the offshore well-head via a “piggy back” line. The process is similar to conventional dehydration units. After passing through a free water separator, MEG is sprayed into the gas stream and flows with the gas as its temperature is reduced by heat exchange or expansion. Since hydrocarbons condense out of the gas phase during the cooling process, a hydrocarbon/MEG separator is required. The MEG is then reconcentrated by distillation and is returned for reinjection into the gas stream.

The design of gas dehydration systems requires an input of the three-phase vapor−liquid−liquid equilibrium (VLLE) data for mixtures which exist under the conditions at the well-head, pipelines, and regeneration units. Since natural gas consists of a large number of components, the usual procedure is to use experimental data on simpler synthetic mixtures to establish the parameters of an equation of state (EoS) model which can then be used in the design process.

This paper is the second one dealing with experimental VLLE in MEG, water, hydrocarbon mixtures. In the first paper, Ashcroft et al.[2] measured the volumes and phase compositions of the quaternary system methane + methyl cyclohexane + MEG + water at 7.0 MPa. In this second paper, the high-pressure equilibrium apparatus has been used to measure VLLE for the quaternary methane + MEG + *n*-octane + water system relevant to the glycol injection plant. The measurements were made over a pressure range from (3.1 to 15.0) MPa and a temperature range from (281 to 363) K, representing the interests of the gas processing industry. As far as the authors are aware, no previously published values are available for this system. In fact, very few measurements have been published on VLLE in MEG, water, and hydrocarbons. Data on related systems containing the hydrate inhibitors MEG and methanol are available in Project 825 of the Gas Processors Association of Tulsa. Specifically, Research Report RR-117 by Chen et al.[3] provides some experimental three-phase data. In a recent study, Folas et al.[4] have applied the cubic-plus-association (CPA) EoS to the correlation and prediction of VLE and VLLE data involving MEG as a hydrate inhibitor.

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Experimental Section

Materials. The source and minimum purity of the materials were as follows: methane (Messer Griesheim, manufacturer's specified purity 0.99995 mol fraction), *n*-octane (Aldrich, 0.995 mass fraction measured by GC), and MEG (Aldrich spectrophotometric grade, manufacturer's specified purity 0.99 mass fraction).

High-Pressure Equilibrium Apparatus. Measurements were made in a type-360 stainless steel equilibrium cell described in detail in the first paper.[2] The cell, designed to operate up to 50 MPa, consisted of two internal cylinders connected via a viewing section and a sampling unit. The system under study was confined between moveable pistons of which the positions could be accurately established by means of vernier scales attached to the locating rods. The maximum cell volume between the pistons was approximately 900 cm^3. The system could be transferred isobarically from one cylinder, through the sampling and viewing sections, into the other cylinder using a double-acting high-pressure displacement pump (Ruska Instruments model 2280). The cell contents could thus be moved through the narrowed viewing section to allow the phases to be identified and their volumes measured. Mixing was achieved by repeatedly pumping the contents of the cell through the connecting line between the cylinders.

Temperature was maintained to ± 0.1 K by circulation of water from a thermostatted bath through a jacket surrounding the cell. Temperatures were measured to an accuracy of ± 0.05 K by thermistors calibrated against short-range mercury-in-glass thermometers (British Standard 791) which themselves had been calibrated by the National Physical Laboratory on the IPTS-68 scale. The equilibrium pressure was measured with an accuracy of ± 0.03 MPa by strain gauge pressure transducers (Sensotec type TJE) calibrated against a dead weight gauge (Budenburg type 80).

Measurements were made by supplying the equilibrium cell with a feed of known composition containing all four components. Mixtures of MEG, water, and *n*-octane were prepared by weighing, and a known amount was transferred to the equilibrium cell. A quantity of methane, under known conditions of volume, pressure, and temperature, was then added to the mixture in the cell. The amount of methane was calculated using the BWR EoS as modified by Starling.[5] The temperature and pressure were set, and the system was brought to equilibrium over a period of several hours. The LLV phase boundaries were identified in the viewing section by moving the system isobarically between the two cylinders within the cell using the calibrated double-acting displacement pump and the piston-locating gauges. Samples were then withdrawn from each of the three phases for analysis.

Analysis. Determination of the minor components in the various phases is difficult. Chen et al.[3] commented on the difficulties of minor component analyses in glycol + water + hydrocarbon mixtures, and they were not able to measure gas-phase glycol concentrations. In the authors' first paper,[2] analysis of the MEG concentrations in the vapor phase of a related system also proved to be just beyond reach. In this second paper, the following improved procedure was developed to enable all the components of the vapor phase to be determined, albeit with different levels of accuracy. The size of the equilibrium cell was such that the isobaric removal of relatively large samples of each phase for analysis was possible. Samples from each liquid phase were expanded through a thermostatted capillary line into an evacuated sample train where separation into liquid and gaseous phases took place, the former being retained in specially designed glass vessels, fitted with PTFE stopcocks, by two cold traps cooled to (200 and 198) K, respectively. The collected liquid was weighed and then analyzed using a GC FID for MEG and hydrocarbons and with a Karl Fischer titration apparatus for water.

The gaseous part of the liquid samples, and the gas phase samples direct from the equilibrium cell, were expanded into a series of evacuated vessels of known volume from which the total amount of substance was determined from the perfect gas equation using the measured low-pressure PVT data. The compositions of the gaseous samples were determined by gas chromatography. To improve the determination of the MEG in the gaseous phase, the following procedure was adopted and applied to most samples from the cell: the sample was expanded from the equilibrium cell to the evacuated vessels via a Tenax absorption tube, where, in addition to the MEG, the liquid hydrocarbons were absorbed by the Tenax substrate. The samples were analyzed on a GC FID (with a polar capillary column, PB-WG-11 (Carbowax), 25 m, ID = 0.25 mm, injector split = 1:60) equipped with specially designed heating equipment by means of which the sample was eluted from the substrate.

Uncertainties. Since the first paper,[2] the analytical improvements, particularly to the vapor phase, have enabled MEG mole fractions as low as $1 \cdot 10^{-7}$ to be detected, thereby allowing measurement of the concentration of MEG in the vapor phase for the first time, albeit with only moderate accuracy. At least five replicate analyses were carried out to determine the reproducibility of the measurements. For methane and *n*-octane mole fractions in the vapor phase, the reproducibility was ± 0.001; for methane and *n*-octane in the *n*-octane liquid phase (L1), the reproducibility was ± 0.005; and for water and MEG in the aqueous liquid phase (L2), the reproducibility was ± 0.005. The reproducibilities of the measurements of the mole fractions of methane and *n*-octane in the aqueous (L2) phase were $\pm 2 \cdot 10^{-4}$ and $\pm 2 \cdot 10^{-6}$, respectively. The mole fractions of MEG and water in the vapor phase and in the *n*-octane liquid phase (L1) were reproducible to about ± 10 % of the reported values. Operational problems caused the loss of samples in a few cases. Tests for accuracy were carried out with binary mixtures of known composition using the methods developed by Ashcroft et al.[6] and Dohrn and Brunner.[7] The accuracy of the mole fractions of methane and *n*-octane in the vapor and L1 phases was found to be between ± 0.001 and ± 0.005. It seems prudent to assign error bands for accuracy of twice the figures given above for reproducibility. In the first paper[2] on four-component mixtures, comparison with the published data of Chen et al.[3] showed good agreement.

Results

A total of 27 sets of P, T, y, x_{L1}, and x_{L2} measurements were obtained covering three different temperatures (281 K, 323 K, and 363 K) and three different pressures (3.1 MPa, 7.1 MPa, and 15.0 MPa) for three different types of feed mixture identified as M1, M2, and M3. The relative proportion of MEG and water was fixed for type M1 and type M2 mixtures at a mass fraction of 0.50 MEG/0.50 water. Type M1 mixtures contained relatively low mole amounts of *n*-octane, whereas type M2 mixtures contained approximately double these amounts of *n*-octane. Type M3 mixtures contained higher amounts of MEG than type M1 mixtures at a mass fraction of 0.83 MEG/0.17 water. Type M3 mixtures contained similar amounts of *n*-octane as type M2 mixtures.

Previous calculations with an EoS had approximately identified the phase envelope and the $P-T$ window within which the

Table 1. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M1 Mixtures (Low MEG) at $T \approx 281$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	281.5	3.10	0.3190	0.9990	0.1441	0.0017
n-octane			0.1071	0.0010	0.8555	$4.0 \cdot 10^{-6}$
MEG			0.1290	$2.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-6}$	0.2257
water			0.4450	$5.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-4}$	0.7726
φ				0.897	0.044	0.058
methane	281.6	7.10	0.4376	0.9984	0.3156	0.0026
n-octane			0.0995	0.0015	0.6842	$6.0 \cdot 10^{-6}$
MEG			0.1039	$2.2 \cdot 10^{-7}$	$3.0 \cdot 10^{-6}$	0.2213
water			0.3589	$3.5 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	0.7761
φ				0.833	0.093	0.074
methane	281.1	15.00	0.5844	0.9956	0.5766	0.0040
n-octane			0.0727	0.0044	0.4232	$1.0 \cdot 10^{-5}$
MEG			0.0772	$2.2 \cdot 10^{-7}$	$2.0 \cdot 10^{-6}$	0.2299
water			0.2657	$3.8 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	0.7660
φ				0.769	0.122	0.082

Table 2. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M1 Mixtures (Low MEG) at $T \approx 323$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	323.2	3.10	0.3548	0.9939	0.1381	0.0019
n-octane			0.1091	0.0033	0.8615	$6.0 \cdot 10^{-6}$
MEG			0.1222	$3.0 \cdot 10^{-7}$	$3.6 \cdot 10^{-5}$	0.2198
water			0.4140	0.0028	0.0004	0.7783
φ				0.927	0.038	0.035
methane	323.2	7.07	0.5061	0.9944	0.2795	0.0023
n-octane			0.0812	0.0032	0.7201	$6.0 \cdot 10^{-6}$
MEG			0.0932	$5.0 \cdot 10^{-7}$	$2.2 \cdot 10^{-5}$	0.2182
water			0.3195	0.0024	$4.0 \cdot 10^{-4}$	0.7795
φ				0.901	0.054	0.045
methane	323.2	14.95	0.5519	0.9940	0.5120	0.0038
n-octane			0.0740	0.0051	0.4877	$8.0 \cdot 10^{-6}$
MEG			0.0842	$1.1 \cdot 10^{-6}$	$4.0 \cdot 10^{-6}$	0.2175
water			0.2899	$9.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	0.7787
φ				0.795	0.116	0.089

Table 3. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M1 Mixtures (Low MEG) at $T \approx 363$ K

Cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	363.2	3.10	0.1542	0.9791	0.1225	0.0018
n-octane			0.1471	0.0114	0.8769	-
MEG			0.1573	$5.0 \cdot 10^{-6}$	$7.1 \cdot 10^{-5}$	0.2250
water			0.5414	0.0095	$5.0 \cdot 10^{-4}$	0.7732
φ				0.762	0.131	0.107
methane	363.2	7.10	0.3143	0.9871	0.2320	0.0023
n-octane			0.1063	0.0088	0.7680	$8.0 \cdot 10^{-6}$
MEG			0.1340	$7.0 \cdot 10^{-6}$	$4.2 \cdot 10^{-5}$	0.2247
water			0.4488	0.0042	$4.0 \cdot 10^{-4}$	0.7730
φ				0.792	0.103	0.104
methane	363.2	15.0	0.4401	0.9848	0.4648	0.0041
n-octane			0.0972	0.0139	0.5351	$8.0 \cdot 10^{-6}$
MEG			0.1041	$2.0 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	0.2219
water			0.3586	0.0012	$4.0 \cdot 10^{-4}$	0.7740
φ				0.728	0.156	0.116

measurements should be executed. The EoS of Gibbons and Laughton,[8] a modification of the Soave−Redlich−Kwong EoS, was used for this purpose. Interaction parameters for the constituent binaries were used.

The results are shown in Tables 1 to 9. In these tables are the mixture type, the feed compositions (z), the pressure and temperature, and the measured mole fractions of the components in the three equilibrium phases where y refers to the gas phase, x_{L1} to the *n*-octane-rich liquid phase, and x_{L2} to the aqueous phase. In addition, the measured equilibrium phase volumes are given as volume fractions φ.

Table 4. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M2 Mixtures (Low MEG) at $T \approx 281$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	280.8	3.10	0.3671	0.9991	0.1451	0.0019
n-octane			0.2684	$9.0 \cdot 10^{-4}$	0.8546	$5.0 \cdot 10^{-6}$
MEG			0.0825	$<1 \cdot 10^{-6}$	$5.9 \cdot 10^{-6}$	0.2225
water			0.2820	$5.0 \cdot 10^{-5}$	$2.0 \cdot 10^{-4}$	0.7755
φ				0.944	0.031	0.025
methane	280.9	7.10	0.6540	0.9989	0.3104	0.0026
n-octane			0.1473	0.0010	0.6894	$7.0 \cdot 10^{-6}$
MEG			0.0448	$<1 \cdot 10^{-6}$	$5.7 \cdot 10^{-6}$	0.2199
water			0.1540	$3.5 \cdot 10^{-5}$	$1.8 \cdot 10^{-4}$	0.7775
φ				0.927	0.043	0.029
methane	281.2	15.00	0.7438	0.9959	0.5440	0.0039
n-octane			0.1138	0.0040	0.4459	$1.0 \cdot 10^{-5}$
MEG			0.0320	$<1 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$	0.2241
water			0.1103	$3.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	0.7719
φ				0.810	0.153	0.037

Table 5. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M2 Mixtures (Low MEG) at $T \approx 323$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	323.4	3.08	0.4573	0.9958	0.1219	0.0018
n-octane			0.2578	0.0030	0.8777	$1.0 \cdot 10^{-5}$
MEG			0.0649	$<1 \cdot 10^{-6}$	$4.0 \cdot 10^{-5}$	0.2188
water			0.2200	0.0012	$3.0 \cdot 10^{-4}$	0.7794
φ				0.880	0.101	0.019
methane	323.4	7.10	0.5307	0.9965	0.2601	0.0025
n-octane			0.2172	0.0030	0.7396	$9.0 \cdot 10^{-6}$
MEG			0.0571	$<1 \cdot 10^{-6}$	$1.4 \cdot 10^{-5}$	0.2201
water			0.1950	$8.0 \cdot 10^{-4}$	$3.0 \cdot 10^{-4}$	0.7774
φ				0.844	0.119	0.036
methane	323.8	15.00	0.6480	0.9926	0.4634	0.0038
n-octane			0.1564	0.0070	0.5363	$1.0 \cdot 10^{-5}$
MEG			0.0440	$1.0 \cdot 10^{-6}$	$4.7 \cdot 10^{-6}$	0.2169
water			0.1515	$3.0 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$	0.7792
φ				0.751	0.200	0.050

Table 6. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M2 Mixtures (Low MEG) at $T \approx 363$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	363.1	3.10	0.3448	0.9761	0.1130	0.0019
n-octane			0.2830	0.0154	0.8859	$6.0 \cdot 10^{-6}$
MEG			0.0851	$4.9 \cdot 10^{-6}$	$7.7 \cdot 10^{-5}$	0.2365
water			0.2870	0.0085	$6.0 \cdot 10^{-4}$	0.7616
φ				0.892	0.078	0.030
methane	363.1	7.10	0.4855	0.9856	0.2407	0.0025
n-octane			0.2269	0.0106	0.7586	$6.0 \cdot 10^{-6}$
MEG			0.0650	$7.4 \cdot 10^{-6}$	$3.2 \cdot 10^{-5}$	0.2246
water			0.2227	0.0039	$6.0 \cdot 10^{-4}$	0.7731
φ				0.817	0.146	0.037
methane	363.1	15.00	0.6220	0.9854	0.4557	0.0039
n-octane			0.1680	0.0135	0.5437	$6.0 \cdot 10^{-6}$
MEG			0.0473	$2.6 \cdot 10^{-5}$	$2.5 \cdot 10^{-5}$	0.2242
water			0.1627	0.0010	$5.0 \cdot 10^{-4}$	0.7719
φ				0.754	0.204	0.042

Discussion

The dehydrating effect of MEG is illustrated in Figure 1 which shows the vapor-phase mole fraction of water at different total pressures as a function of temperature for type M1 mixtures. To illustrate the dehydrating effect, a few points are plotted for the binary methane + water system at 4.0 MPa (no MEG). It was observed that published values for the methane + water binary show a wide scatter. The values shown are those of Folas et al.[9] who have also commented on the considerable variation in published data on the binary system. Figure 2 shows

Table 7. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M3 Mixtures (High MEG) at $T \approx 281$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	281.0	3.10	0.3159	0.9993	0.1662	0.0022
n-octane			0.3991	$6.0 \cdot 10^{-4}$	0.8336	$5.0 \cdot 10^{-5}$
MEG			0.1663	$6.0 \cdot 10^{-7}$	$5.9 \cdot 10^{-5}$	0.5743
water			0.1187	$4.0 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$	0.4235
φ				0.767	0.201	0.032
methane	280.0	7.10	0.4681	0.9992	0.3308	0.0037
n-octane			0.3204	$7.0 \cdot 10^{-4}$	0.6691	$4.0 \cdot 10^{-5}$
MEG			0.1233	$6.0 \cdot 10^{-7}$	$3.5 \cdot 10^{-5}$	0.5727
water			0.0882	$3.5 \cdot 10^{-5}$	$7.0 \cdot 10^{-5}$	0.4235
φ				0.707	0.251	0.042
methane	281.0	15.00	0.5960	0.9957	0.4163	0.0047
n-octane			0.2429	0.0043	0.5837	$2.0 \cdot 10^{-5}$
MEG			0.0938	$6.0 \cdot 10^{-7}$	$3.6 \cdot 10^{-5}$	0.5745
water			0.0674	$4.0 \cdot 10^{-5}$	$5.0 \cdot 10^{-5}$	0.4208
φ				0.650	0.290	0.061

Table 8. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M3 Mixtures (High MEG) at $T \approx 323$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	323.2	3.10	0.3613	0.9987	0.1101	0.0022
n-octane			0.3844	0.0010	0.8896	-
MEG			0.1483	$2.2 \cdot 10^{-7}$	$5.5 \cdot 10^{-5}$	0.5792
water			0.1060	$3.0 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	0.4186
φ				0.749	0.200	0.051
methane	323.2	7.10	0.4816	0.9980	0.2685	0.0040
n-octane			0.3060	0.0019	0.7312	$5.1 \cdot 10^{-5}$
MEG			0.1241	$5.0 \cdot 10^{-7}$	$3.5 \cdot 10^{-5}$	0.5935
water			0.0883	$1.2 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	0.4024
φ				0.692	0.256	0.052
methane	323.2	15.00	0.6335	0.9937	0.4489	0.0070
n-octane			0.2194	0.0063	0.5509	$3.2 \cdot 10^{-5}$
MEG			0.0858	$8.6 \cdot 10^{-7}$	$3.4 \cdot 10^{-5}$	0.5818
water			0.0612	$5.6 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$	0.4112
φ				0.807	0.157	0.036

Table 9. Compositions (Mole Fractions) of the Feed and Equilibrium Phases and Relative Phase Volumes (φ) for the System Methane + *n*-Octane + MEG + Water for Type M3 Mixtures (High MEG) at $T \approx 363$ K

cmpt	T/K	P/MPa	z	y	x_{L1}	x_{L2}
methane	363.2	3.10	0.3935	0.9834	0.1207	0.0033
n-octane			0.2248	0.0112	0.8790	$6.5 \cdot 10^{-5}$
MEG			0.2264	$2.3 \cdot 10^{-6}$	$1.1 \cdot 10^{-4}$	0.5909
water			0.1554	0.0053	$2.8 \cdot 10^{-4}$	0.4058
φ				0.793	0.175	0.033
methane	363.2	7.10	0.4436	0.9918	0.2530	0.0052
n-octane			0.3321	0.0065	0.7467	$5.5 \cdot 10^{-5}$
MEG			0.1310	$1.8 \cdot 10^{-5}$	$7.2 \cdot 10^{-5}$	0.5720
water			0.0933	0.0016	$2.3 \cdot 10^{-4}$	0.4224
φ				0.728	0.231	0.041
methane	363.2	15.00	0.6655	0.9858	0.4579	0.0107
n-octane			0.2012	0.0137	0.5419	$3.5 \cdot 10^{-5}$
MEG			0.0776	$1.9 \cdot 10^{-5}$	$4.5 \cdot 10^{-5}$	0.5658
water			0.0557	$5.0 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	0.4234
φ				0.683	0.274	0.043

a similar plot for type M3 mixtures which contain a higher concentration of MEG in the feed. The greater dehydrating effect of this higher concentration can be seen. The data in Tables 1 to 9 also show that varying the *n*-octane composition of the feed mixtures has relatively little influence on the water concentrations in the vapor phase.

To predict the losses of MEG in processes for the dehydration of natural gas, the concentrations of MEG in the vapor phase are of interest to the gas industry. Very few measurements are available in the literature, and none exist for three-phase systems.

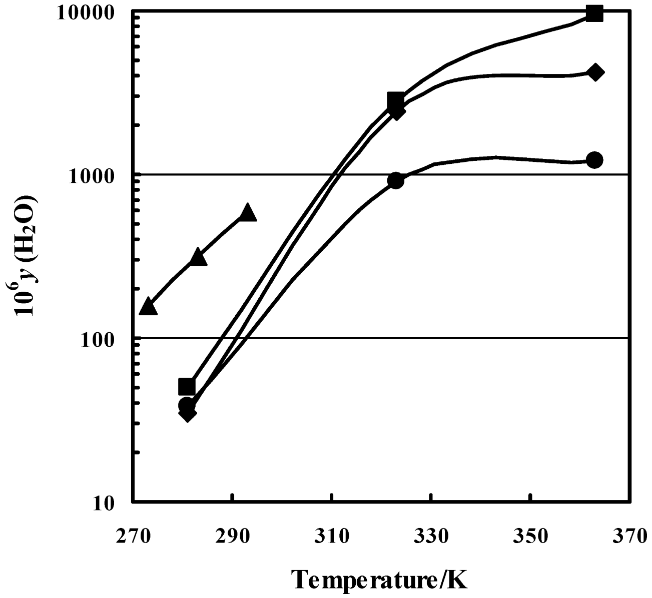

Figure 1. Vapor-phase mole fractions of water for type M1 mixtures (low MEG) at ■, 3.1 MPa; ◆, 7.1 MPa; and ●, 15.0 MPa compared with published data[9] for the methane + water system at ▲, 40 bar.

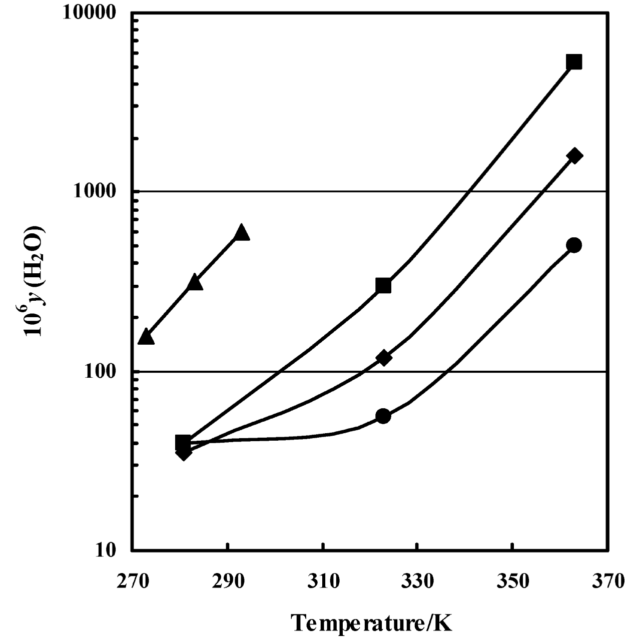

Figure 2. Vapor-phase mole fractions of water for type M3 mixtures (high MEG) at ■, 3.1 MPa; ◆, 7.1 MPa; and ●, 15.0 MPa compared with published data[9] for the methane + water system at ▲, 40 bar.

The values for type M1 mixtures from Tables 1 to 3 are plotted in Figure 3 as equilibrium *K*(MEG) values (where *K*(MEG) = mole fraction MEG in the vapor phase/mole fraction in the aqueous (L2) phase) in comparison with recent two-phase VLE data from Folas et al.[10] for the ternary methane + MEG + water system. Despite the differences in the systems studied and the relatively large uncertainties of the measurements, there is reasonable agreement between the *K*(MEG) values which show a general increase with increasing pressure and temperature.

A further important quantity is the solubility of the hydrocarbons in the aqueous (L2) phase since strong legislation exists for the levels of hydrocarbons which may be discharged to the environment. The solubilities of methane and *n*-octane in the aqueous phase are considerably enhanced by the presence of MEG. Figure 4 illustrates the extent of this effect for methane

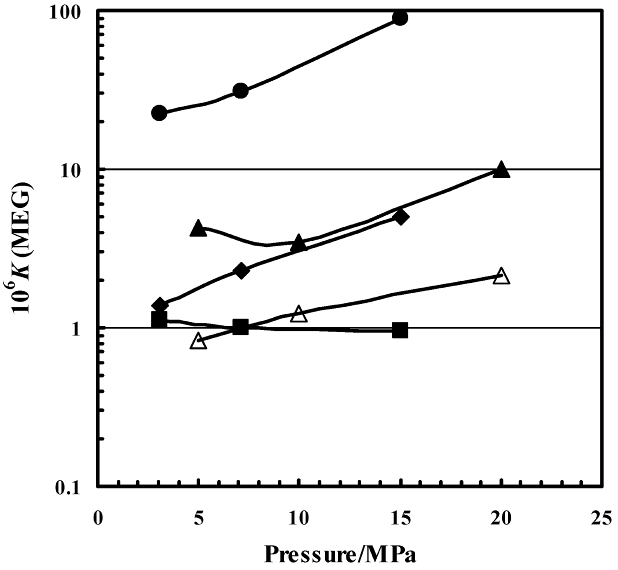

Figure 3. Vapor−liquid equilibrium *K*-values for MEG (= mole fraction MEG in the vapor phase/mole fraction in the aqueous (L2) phase) for type M1 mixtures at ■, 281 K; ◆, 323 K; and ●, 363 K compared with published VLE data[10] at ▲, 278 K and △, 298 K for the ternary system methane + MEG + water.

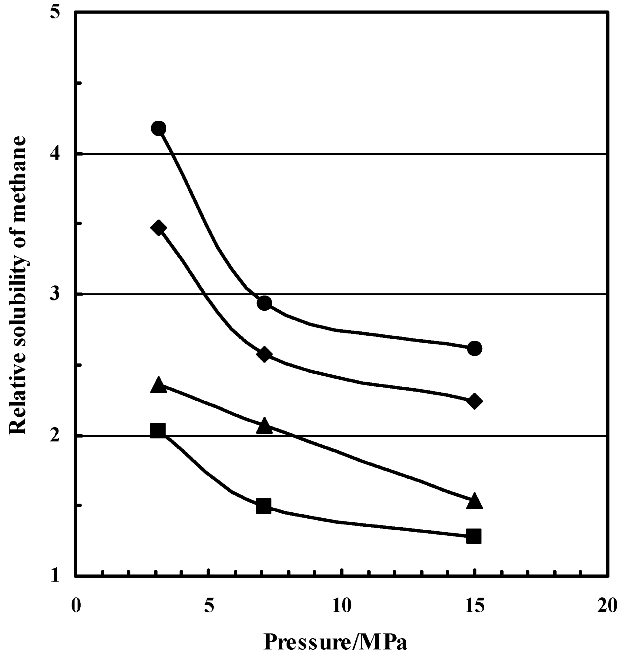

Figure 4. Solubility of methane in the aqueous (L2) phase for type M2 mixtures (low MEG) at ■, 281 K; ◆, 323 K; and ●, 363 K and for a type M3 mixture (high MEG) at ▲, 281 K relative to methane solubility[11] in pure water at the same *T* and *P*.

in the form of the ratio of the measured mole fraction of methane in L2 to the mole fraction in pure water at the same temperature and methane partial pressure. The latter data were taken from the equation of Battino given in Clever and Young.[11] This figure shows that the enhanced solubility of methane is greater at higher temperatures, decreases somewhat with increasing pressure, and is greater at higher levels of MEG as shown by comparing type M3 mixtures with type M2.

In Figure 5, some solubilities of *n*-octane in the aqueous (L2) phase are shown relative to solubilities in pure water (Tsonopoulos[12]) at the same temperature but at atmospheric pressure. The values are illustrated for three type M2 mixtures (low MEG) at different temperatures and one type M3 mixture (high MEG).

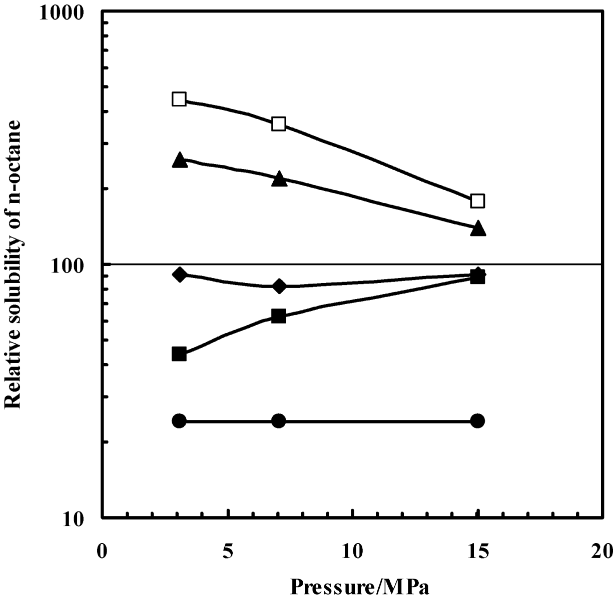

Figure 5. Solubility of *n*-octane in the aqueous (L2) phase for type M2 mixtures (low MEG) at ■, 281 K; ◆, 323 K; and ●, 363 K and for type M3 mixtures (high MEG) at □, 281 K and ▲, 363 K relative to *n*-octane solubility[12] in pure water at the same *T*.

The solubility of *n*-octane is considerably increased by the presence of MEG, and as expected, the effect is larger at higher levels of MEG. The solubility is greater at higher temperatures, but the effect of pressure is probably insignificant.

Conclusion

Experimental measurements, reported in this paper, on three-phase equilibria in the system methane + *n*-octane + MEG + water are relevant to the dehydration of gas mixtures by MEG in-line injection systems. The results show that changing the MEG/water ratio of the feed mixture has a strong influence on the water concentration in the gas phase. On the other hand, a change in the hydrocarbon content has relatively little influence on the equilibrium. Increasing the concentration of water in the MEG/water feed results in a considerable decrease in the MEG mole fraction in the *n*-octane liquid phase. For MEG dehydration processes, this means that the loss of hydrocarbons can be reduced when using optimized (low) MEG concentrations. As expected, increasing the temperature results in a higher water content in the gas phase, whereas increasing the pressure results in a lower water content. The equilibrium data for methane and *n*-octane in the aqueous phase should be of interest for the prediction of hydrocarbons discharged into the environment after the generation of wet MEG.

Nomenclature

K(MEG)	mole fraction MEG in the vapor phase/mole fraction in the aqueous (L2) phase
EoS	equation of state
L1	*n*-octane-rich phase
L2	water-rich (aqueous) phase
MEG	monoethylene glycol
M1 and M2	feed mixtures containing MEG/water of 0.50 mass fraction MEG
M3	feed mixtures containing MEG/water of 0.83 mass fraction MEG
P	total pressure
T	temperature
TEG	triethylene glycol

VLE	vapor−liquid equilibrium
VLLE	vapor−liquid−liquid equilibrium
x	liquid phase mole fraction
y	vapor phase mole fraction
z	feed mole fraction
φ	phase volume fraction

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Literature Cited

(1) Manning, F. S.; Thompson, R. E. *Oilfield Processing of Petroleum*; Natural Gas, PennWell Publishing Company: Tulsa, OK, 1991; Vol. I.

(2) Ashcroft, S. J.; Vollmer, H.; Brunner, G.; Sweeney, C. W. Apparatus for high-pressure three-phase equilibria in (methane+methylcyclohexane+ethan-1,2-diol+water). *J. Chem. Thermodyn.* **1995**, *27*, 969–978.

(3) Chen, C. J.; Ng, H.-J.; Robinson, D. B. *The Solubility of Methanol or Glycol in Water-Hydrocarbon Systems.* GPA Research Report RR-117, Gas Processors Association: Tulsa, OK, 1988.

(4) Folas, G. K.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. Vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibrium of binary and multicomponent systems with MEG. Modeling with the CPA EoS and an EoS/G^E Model. *Fluid Phase Equilib.* **2006**, *249*, 67–74.

(5) Starling, K. E. *Fluid Properties for Light Petroleum Systems*; Gulf Publishing Company: Houston, TX 1973.

(6) Ashcroft, S. J.; Shearn, R. B.; Williams, G. J. J. A visual equilibrium cell for multiphase systems at pressures up to 690 bar. *Chem. Eng. Res. Des.* **1983**, *61*, 51–55.

(7) Dohrn, R.; Brunner, G. Phase equilibria in ternary and quaternary systems of hydrogen, water and hydrocarbons at elevated temperatures and pressures. *Fluid Phase Equilib.* **1986**, *29*, 535–544.

(8) Gibbons, R. M.; Laughton, A. P. An equation of state for polar and non-polar substances and mixtures. *J. Chem. Soc, Faraday Trans. II* **1984**, *80*, 1019–1038.

(9) Folas, G. K.; Froyna, E. W.; Lovland, J.; Kontogeorgis, G. M.; Solbraa, E. Data and prediction of water content of high pressure nitrogen, methane and natural gas. *Fluid Phase Equilib.* **2007**, *252*, 162–174.

(10) Folas, G. K.; Berg, O. J.; Solbraa, E.; Fredheim, A. O.; Kontogeorgis, G. M.; Michelsen, M. L.; Stenby, E. H. High-pressure vapor-liquid equilibria of systems containing ethylene glycol, water and methane. Experimental measurements and modeling. *Fluid Phase Equilib.* **2007**, *251*, 52–58.

(11) IUPAC Solubility Data Series. *Methane*; Clever, H. L., Young, C. L., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. 27/28.

(12) Tsonopolous, C. Thermodynamic analysis of the mutual solubilities of normal alkanes and water. *Fluid Phase Equilib.* **1999**, *156*, 21–33.

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