Phase Equilibria in the System Water-Methyldiethanolamine-Propane

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Aqueous solutions of alkanolamines are commonly used to strip acid gases (CO_2 and H_2S) from hydrocarbon streams. Processes for stripping acid gases from gaseous streams are well understood; however, the application to liquids is not as advanced. Experimental data available are scarce for systems containing aqueous amine solutions and the constituents of liquefied petroleum gases. To this end, new data are presented for the equilibria in the system propane-water-methyldiethanolamine (MDEA). A knowledge of the phase behavior in this system is required to model the equilibria encountered in the more complex systems of industrial importance.

This work is a comprehensive study of the phase equilibria in the system propane-3 M MDEA, including vapor-liquid, liquid-liquid, and vapor-liquid-liquid equilibria. Experimental measurements were made for temperatures between 0 and 150°C and pressures up to 20 MPa. The data were correlated using the Stryjek-Vera modification of the Peng-Robinson equation of state. In addition, a composition-dependent mixing rule was required to fit the data adequately.

Introduction

Aqueous solutions of alkanolamines have been used for many years to strip acid gases (carbon dioxide and hydrogen sulfide) from natural gas. One amine that has received much attention recently is methyldiethanolamine (MDEA). MDEA, a tertiary amine, has the advantage of being more selective for H_2S removal than conventional amines such as monoethanolamine (MEA) or diethanolamine (DEA). Its selectivity arises because H_2S reacts much faster than CO_2 with MDEA. MDEA has the disadvantage of being more expensive than the conventional amines.

Liquefied petroleum gas (LPG) is a valuable by-product of natural gas processing. LPG consists of propane and butane; though, it is often contaminated with unwanted components. Aqueous amine solutions are used to strip the acid gases from LPG. Thus an understanding of the phase behavior of systems containing propane, butane, water and amines are required for the design and operation of these plants. An additional problem with separating hydrogen sulfide from propane is the formation of an azeotrope. This makes separation by binary distillation impossible. Thus stripping H_2S from the propane with an aqueous amine solution is an attractive alternative. Even though acid gases are currently being stripped from LPG in commercial plants, few experimental data exist for the equilibria between sour LPG and aqueous amines. The design of these plants is often based on experience, rather than rational procedures, with all the problems that this embodies (Holmes et al., 1984).

The goal of this article is to study the phase equilibria in the system propane-3 M MDEA, including vapor-liquid equilibrium (VLE), liquid-liquid equilibrium (LLE), and vapor-liquid-liquid equilibrium (VLLE). The following nomenclature will be used to designate the different phases: L_A (aqueous liquid), L_P (propane-rich liquid), V (vapor), and H (hydrate).

Previous Experimental Work

The definitive study of the system propane-water was done by Kobayashi and Katz (1953). This was a thorough study that included VLE, LLE, and VLLE. De Loos et al. (1980) also studied the system propane-water, but all their data are outside the range of temperature of interest in this study. In a thorough investigation of the phase behavior of hydrocarbon-water systems, Brunner (1990) measured the pressure and temperature along VLLE locus for the system propane-water, including the three-phase critical end point. Recently, Harmens and Sloan

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(1990) presented a new interpretation of the phase behavior of this system over the entire range of pressure and temperature.

Very little data exist for the binary system water-MDEA. Recently, Xu et al. (1991) measured the boiling points for mixtures of MDEA and water.

No data exist for the binary system MDEA-propane. Finally, there have been no previous investigations of the ternary system either.

Experimental Work

The equilibrium of a ternary mixture of water-MDEA-propane was studied in this investigation. A 3 M aqueous MDEA solution (at room conditions, 34.67 wt. % or 7.42 mol %) was employed.

Apparatus and procedure

The equipment and procedure used in this experiment are well-established (Jou et al., 1985; Jou et al., 1987). Briefly, the apparatus consisted of a cell and a recirculation pump housed in a temperature controlled air bath. The cell was a Jerguson liquid level gauge. A 250-cm^3 reservoir was attached to the top of the cell to ensure that there was sufficient material in the system. The recirculation pump was a magnetic piston pump similar to one devised by Ruska et al. (1970). Mixing was achieved by drawing the L_P or V phase off the top of the reservoir and pumping it into the bottom through the aqueous phase. Sampling lines are connected to ports along the cell such that a portion of the fluids can be withdrawn and analyzed. The equipment with the exception of the pump piston was constructed from 316 stainless steel. Since the piston had to be ferromagnetic, it was constructed from Carpenter 450.

The temperature of the contents of the cell was measured using an iron-constantan thermocouple and the pressure with a Bourdon tube gauge. The thermocouple was calibrated against a platinum resistance thermometer and the temperature is known to be ± 0.1°C. The pressure gauges were calibrated against a dead-weight gauge and were accurate to within 0.1% of full scale.

The analysis of the phases also employed well-established methods. The concentration of the propane in the aqueous phase was obtained by the procedure described by Jou et al. (1987). Briefly, a sample of the aqueous phase was withdrawn into a sample bomb. The mass of the sample was measured and then it was degassed under vacuum. The volume of the hydrocarbon released from the liquid was measured and the moles of propane were calculated. Finally, the composition of the L_P and V phases were determined using gas chromatography (Jou et al., 1987).

Results

The three-phase equilibria for the system propane-3 M MDEA are listed in Table 1. The third column in this table indicates the nature of the third phase, which is propane-rich (an aqueous phase is always present). The points labeled "dew" are where a propane-rich liquid begins to form, which is in equilibrium with an aqueous liquid and a vapor. Those marked "bub" are where a vapor forms, which is in equilibrium with two liquids.

For a binary system existing in three phases, the phase rule states that there is only one degree of freedom. Thus, for a binary system, the three-phase locus is a curve in the P-T plane. This will be demonstrated later for the system propane-water. On the other hand, for a ternary system existing in three-phases, the phase rule says that there are two degrees of freedom. Therefore, a three component system has a three-phase region in the P-T plane. From the data in Table 1 the region for propane-water-MDEA is very narrow in pressure.

The compositions of the coexisting phases at 25, 40, 50, 75, 100, 125 and 150°C are listed in Table 2. Some of these data are in the vapor-liquid region, some are in the liquid-liquid, and the remainder are at temperatures where only two phases exist. The third column in Table 2 indicates the nature of the propane-rich phase. At temperatures above 97.4°C (the three-phase critical end point), the L_P phase does not exist. Thus in Table 2 the second phase at these conditions is called a vapor.

From Table 2 it can be seen that very little of the MDEA is in the propane-rich phases; the maximum concentration is only 0.180 mol%. Thus, a large error does not arise from the assumption that there is no MDEA in the vapor or the propane-rich liquid.

The three-phase critical end point for the ternary mixture found in this study was 97.4°C and 4,380 kPa. For the binary system propane-water Kobayashi and Katz (1953) found the three-phase critical end point to be 96.5°C and 4,390 kPa and Brunner (1990) found 96.5°C and 4,260 kPa. Thus the critical

Table 1. Compositions of the Phases Along the Three-Phase Boundary for the System Propane-Water-MDEA

			Aq. Phase	Propane-Rich Phase	
Temp. (°C)	Pres. (kPa)	Phase	Mole Frac. C_3H_8 (10^4)	Mole Frac. H_2O (10^2)	Mole Frac. MDEA (10^4)
0	470	dew	4.18	0.138	—
	477	bub	4.08	0.0172	0.0136
25	960	dew	5.01	0.302	0.0055
	970	bub	4.98	0.0521	0.0735
40	1,390	dew	5.50	0.476	0.0124
	1,420	bub	5.46	0.0959	0.218
50	1,740	dew	6.01	0.630	0.0268
	1,780	bub	5.97	0.150	0.339
60	2,100	dew	6.65	0.776	—
	2,160	bub	6.60	0.202	—
75	2,870	dew	7.98	1.02	0.193
	2,940	bub	7.93	0.336	1.12
85	3,460	dew	9.26	1.22	0.491
	3,520	bub	9.22	0.453	1.88
90	3,800	dew	9.89	1.31	0.829
	3,850	bub	9.86	0.542	2.02
95	4,180	dew	11.62	1.27	1.31
	4,220	bub	11.65	0.642	1.93
96.4	4,300	dew	12.09	1.22	—
	4,320	bub	12.04	0.806	—
97.4	4,380	CP	12.53	1.15	1.72

dew = dew point
bub = bubble point
CP = critical point

Table 2. Compositions of the Coexisting Phases for the System Propane-Water-MDEA

Temp. (°C)	Pres. (kPa)	Phase	Aq. Phase Mole Frac. C_3H_8 (10^4)	Propane-Rich Phase Mole Frac. H_2O (10^2)	Propane-Rich Phase Mole Frac. MDEA (10^4)
0	126	vapor	1.26	—	—
	200	vapor	2.00	0.292	—
	280	vapor	2.63	—	—
	1,000	liquid	4.21	0.0175	0.0178
	3,000	liquid	4.28	0.0223	0.0176
	6,000	liquid	4.28	0.0194	0.0203
	10,000	liquid	4.43	0.0156	0.0285
	15,000	liquid	4.63	0.0217	—
	20,000	liquid	4.64	0.0260	0.0356
25	104	vapor	0.622	—	—
	171	vapor	1.01	—	—
	273	vapor	1.66	—	—
	550	vapor	3.15	0.543	—
	2,410	liquid	5.05	—	—
	3,000	liquid	5.15	0.0543	0.103
	4,800	liquid	5.02	—	—
	6,750	liquid	5.20	0.0547	0.132
	9,390	liquid	5.11	0.0548	0.130
	12,690	liquid	5.14	0.0634	0.175
	15,460	liquid	5.58	0.0673	0.140
	19,800	liquid	5.73	0.0621	0.147
40	112	vapor	0.546	—	—
	269	vapor	1.35	—	—
	811	vapor	3.65	—	—
	2,610	liquid	5.49	—	—
	4,650	liquid	5.63	—	—
	6,810	liquid	5.82	—	—
	10,000	liquid	5.94	—	—
	13,500	liquid	6.02	—	—
	17,000	liquid	5.94	—	—
	20,120	liquid	6.25	—	—
50	101	vapor	0.441	—	—
	274	vapor	1.28	—	—
	550	vapor	2.51	1.98	—
	910	vapor	3.79	1.26	—
	3,980	liquid	5.98	0.144	0.428
	6,500	liquid	6.09	0.167	0.400
	10,420	liquid	6.52	0.147	0.506
	14,270	liquid	6.48	0.152	0.529
	17,170	liquid	6.56	0.159	0.537
	19,950	liquid	6.68	0.145	0.612
75	118	vapor	0.371	—	—
	179	vapor	0.648	—	—
	285	vapor	1.09	—	—
	550	vapor	2.25	5.84	0.360
	860	vapor	3.17	—	—
	2,120	vapor	6.59	1.44	0.0967
	4,220	liquid	8.30	—	—
	6,580	liquid	8.28	0.336	1.38
	9,160	liquid	8.49	0.306	1.83
	11,860	liquid	8.80	0.322	1.86
	13,880	liquid	8.77	0.345	1.63
	16,810	liquid	8.96	0.376	1.97
	19,640	liquid	8.99	0.388	1.86
100	194	vapor	0.452	49.33	2.28
	270	vapor	0.817	—	—
	380	vapor	1.30	—	—
	550	vapor	2.41	17.57	0.889
	970	vapor	3.53	9.20	—
	1,550	vapor	5.71	5.79	—
	2,380	vapor	7.68	3.84	—
	4,520	vapor	12.27	1.53	1.69
	6,680	vapor	12.29	0.785	3.28
	9,540	vapor	12.77	0.754	4.44
	13,230	vapor	12.95	0.756	5.40
	15,540	vapor	13.52	0.780	5.71
	18,830	vapor	14.19	0.818	5.97
125	317	vapor	0.529	71.27	—
	452	vapor	1.22	44.63	4.01
	1,230	vapor	4.66	16.67	1.66
	2,720	vapor	9.76	8.14	1.04
	4,550	vapor	14.34	4.00	1.28
	6,690	vapor	17.10	2.83	3.44
	9,090	vapor	17.89	1.87	8.68
	12,310	vapor	19.05	1.77	10.99
	15,760	vapor	19.84	1.63	11.30
	18,740	vapor	20.51	—	—
150	545	vapor	0.622	—	—
	707	vapor	1.57	—	—
	1,290	vapor	4.71	33.01	4.54
	2,690	vapor	11.26	15.83	2.21
	4,510	vapor	17.36	9.21	1.56
	6,650	vapor	22.56	7.18	5.89
	9,920	vapor	26.24	4.23	11.39
	12,750	vapor	28.37	3.20	17.17
	15,540	vapor	29.62	2.74	18.03
	18,370	vapor	30.88	—	—

point for the ternary mixture is only slightly different from that of the binary.

The propane–water binary has a H-L_A-L_P-V quadruple point at 5.7°C and 567 kPa according to Kobayashi and Katz (1953). No hydrate was observed for the ternary mixture at temperatures as low as 0°C. Thus, the presence of the amine inhibited the formation of the hydrate.

Correlation of the Data

It is desirable to correlate the data with a reliable model such as an equation of state. Cubic equations of state have become the workhorses of the process modeling industry. Their combination of simplicity and accuracy makes them very attractive. One of the most popular equations was proposed by Peng and Robinson (1976a) (the PR equation). It yields excellent results for petroleum systems (those containing light hydrocarbons and a few associated nonhydrocarbons). Unfortunately the PR equation cannot be used for polar compounds.

The PRSV equation of state

Recently Stryjek and Vera (1986a) proposed an extension of the PR equation (the PRSV equation), which accurately correlates the vapor pressure of polar substances. This equation should be useful for correlating the fluid phase equilibria in systems containing polar components. The selection of the PRSV equation over other equations, which accurately correlate the vapor pressure of polar substances, is a somewhat arbitrary one. Any of the modified forms of the PR equation (or the Soave, 1972, equation, for example, Mathias, 1983)

Table 3. Pure Component Parameters for the PRSV Equation of State

Comp.	T_c(K)	P_c(kPa)	ω	κ_1
Water	647.3	22,090	0.3440	−0.06635
Propane	369.8	4,250	0.1542	0.03136
MDEA	680.7	4,053	1.1250	−1.09940

should yield similar results provided they accurately fit the pure component vapor pressure.

The PRSV equation is:

$$P = RT/(v-b) - a[T]/(v^2+2bv-b^2) \tag{1}$$

$$a[T_c] = 0.45724\ R^2T_c^2/P_c \tag{2}$$

$$a[T] = a[T_c]\alpha \tag{3}$$

$$\alpha = [1+\kappa(1-T_R^{1/2})]^2 \tag{4}$$

$$\kappa = \kappa_0 + \kappa_1(1+T_R^{1/2})(0.7-T_R) \tag{5}$$

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.019654\omega^3 \tag{6}$$

$$b = 0.07780\ RT_c/P_c \tag{7}$$

where κ_1 is an empirical parameter. For most substances κ_1 is set equal to zero for reduced temperatures greater than 0.7, however, water is an exception to this rule. For all substances, κ_1 is set equal to zero for temperatures greater than the critical temperature.

The pure component parameters for water and propane were obtained from Stryjek and Vera (1986a). MDEA was not listed in their table, nor in a later table of Proust and Vera (1989). The parameters for MDEA were obtained in this study as follows. The critical point of MDEA was estimated using Lydersen's correlation (Reid et al., 1977) and the acentric factor was estimated from the Lee-Kesler correlation (Reid et al., 1977). With the estimated critical point and acentric factor for MDEA, κ_1 was obtained by fitting the vapor pressure data of Daubert and Hutchinson (1990). As with water, κ_1 for MDEA was *not* set equal to zero for T_R between 0.7 and 1. Table 3 summarizes the pure component parameters used in this study.

To apply a cubic equation of state to a mixture a set of mixing rules is required. For a van der Waals-type equation the following rules are usually applied:

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2}(1-\delta_{ij}) \tag{8}$$

$$b = \sum_i x_i b_i \tag{9}$$

These mixing rules work well for petroleum systems; but, they do not work for systems containing a polar component such as water. Experience has shown that at least one additional parameter per binary pair (possibly temperature-dependent) is usually required. One such mixing rule was proposed by Stryjek and Vera (1986b) (also see Panagiotopoulos and Reid, 1986).

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2}(1 - x_i k_{ij} - x_j k_{ji}) \tag{10}$$

This mixing rule will be used here. In general, $k_{ij} \neq k_{ji}$; but, the original mixing rule, Eq. 8, is recovered if $k_{ij} = k_{ji}$. Equation 9 was retained for the mixing rule for the covolume.

We are aware of the recent discussion in the literature regarding problems with composition-dependent mixing rules such as Eq. 10 (Michelsen and Kistenmacher, 1990; Mathias et al., 1991; and Schwartzentruber and Renon, 1991). However, this problem appears to be important when components with similar properties are involved. Such is not the case in this study. Also, the main goal of this work was to obtain a satisfactory fit of the new experimental data. As will be demonstrated, such a fit was obtained. Notwithstanding, caution should be exercised if the correlation is extrapolated to multicomponent mixtures.

The interaction parameters of water-propane were obtained from the binary data only. The suitability of this approach to the binary propane-water system will be discussed later in this paper. To obtain an accurate correlation of the propane-water data, it was necessary to make one of the interaction parameters in Eq. 10 a function of temperature.

The other four interaction parameters were obtained by fitting the bubble points of the ternary mixture. To calculate the bubble points, the ternary mixture was treated as a pseudo-binary. The amount of propane in the liquid was specified and the ratio of MDEA to water was set equal to that of 3 M solution (12.475 mol H_2O/mol MDEA). Thus the liquid-phase composition was completely specified. It was determined that the interaction parameters for H_2O-MDEA had the largest influence on the calculation. Thus, they were fit first. Both of these parameters were functions of temperature. Then the C_3H_8-MDEA and MDEA-C_3H_8 parameters were obtained using the previously determined interaction parameters for H_2O-MDEA. It was determined that a satisfactory fit was obtained by setting $k_{C_3H_8\text{-MDEA}} = 0$. The 100°C isotherm was not used to find the optimum interaction parameters due to the prediction of a "false" third phase for some combinations of interaction parameters. Nonetheless, the optimum interaction parameters do not predict this false third phase. To obtain the desired fit, it was necessary to allow the interaction parameters to be a function of temperature.

The average absolute error in the predicted bubble point pressure is 3.0% excluding the 100°C isotherm, and it is 4.2% when it is included [absolute error, $AE = |$calculated

Table 4. Binary Interaction Parameters

Comp. 1	Comp. 2	k_{12}	k_{21}
Water	Propane	$0.4794 - 205.59/T$	0.570
Water	MDEA	$-0.0841 - 82.93/T$	$-0.2392 + 41.46/T$
Propane	MDEA	0	$8.0310 - 5684.313/T + 9.97429\times10^5/T^2$

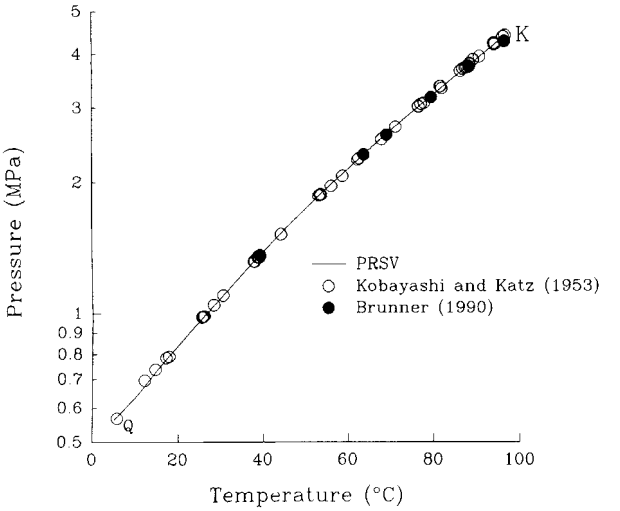

Figure 1. Liquid-liquid-vapor locus for the propane-water system.

K, three-phase critical end point; *Q*, H-L_P-L_A-V quadruple point.

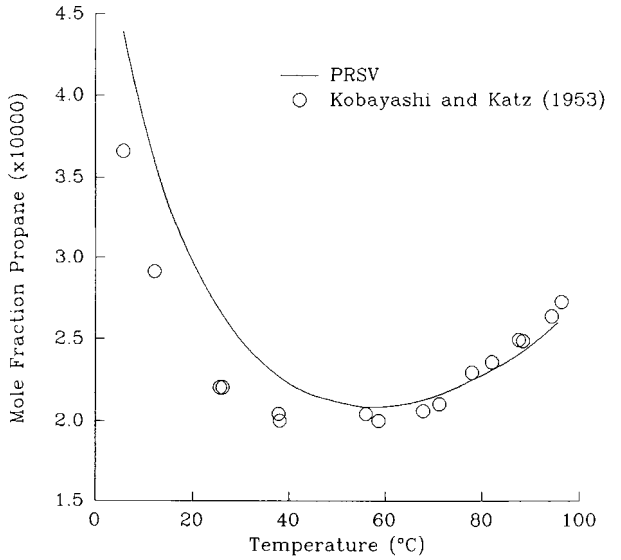

Figure 3. Composition of the aqueous phase along the L_P-L_A-V locus for the system propane-water.

Data from Kobayashi and Katz (1953), curve from PRSV calculation.

−experimental|/experimental; average absolute error, $AAE = \left(\sum_{i=1}^{NP} AE_i\right)/NP$ where NP is the number of points]. The maximum absolute error is 10.8% for the isotherms other than 100°C. Table 4 summarizes the interaction parameters used in this study. More discussion of the calculated bubble point is included later in this paper.

The system propane-water

Calculations for the propane-water system are done to decide whether the equation of state approach would be applicable to the ternary system. The phase equilibria for the propane-water system is complex, exhibiting liquid-liquid immiscibility and the formation of a hydrate. However, only equilibria involving fluid phases will be examined here.

Since the three-phase equilibrium is very important for the description of the equilibria in the system propane-water it will be discussed first. Figure 1 shows the predicted and experimental pressure-temperature locus along the VLLE curve. This locus begins at the H-L_A-L_P-V quadruple point (marked Q on the figure) and extends to the three-phase critical point (marked K on the figure) where the L_p and V phases become identical. Figures 2 and 3 show the compositions of the coexisting phases;

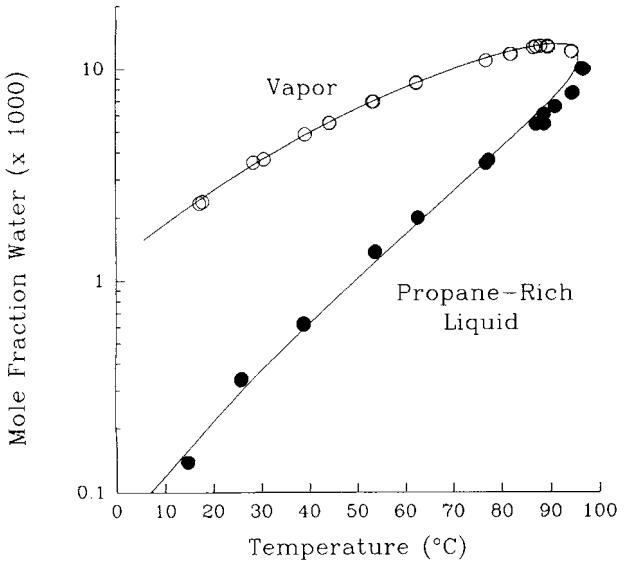

Figure 2. Composition of the propane-rich phases along the L_P-L_A-V locus for the system propane-water.

Data from Kobayashi and Katz (1953), curve from PRSV calculation.

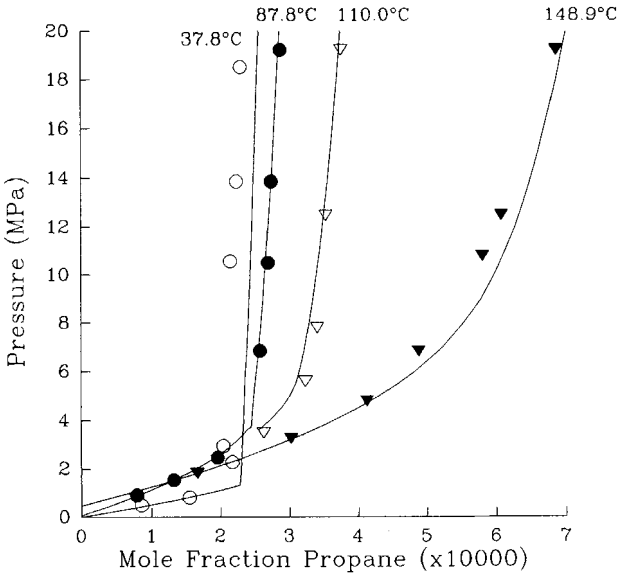

Figure 4. Mole fraction propane in the aqueous phase for the system propane-water.

Data from Kobayashi and Katz (1953), curve from PRSV calculation.

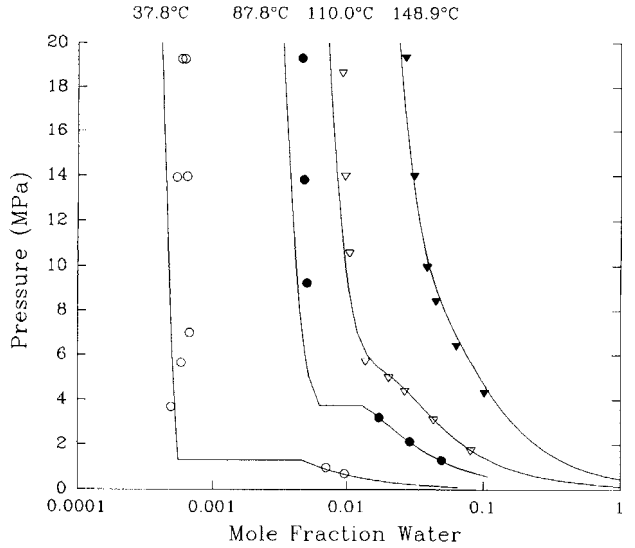

Figure 5. Mole fraction water in the propane-rich phases for the system propane-water.

Data from Kobayashi and Katz (1953), curve from PRSV calculation.

the propane-rich phases (L_P and V), shown on Figure 2 and the aqueous phase, shown on Figure 3. From these figures it can be seen that there is very good agreement between the experimental and the predicted behavior for this binary system along the three-phase locus.

Figures 4 and 5 show the VLE and LLE for four isotherms: 37.8, 87.8, 110.0 and 148.9°C. Figure 4 shows the aqueous phase and Figure 5 the propane-rich phases (L_P and V). Although the calculations for the two figures were performed simultaneously, they are presented separately for clarity. Again, the agreement is good. The plateaus on Figure 5 at 37.8 and 87.8°C are the three-phase points. An additional phase envelope, L_p-V, would extend from this plateau and intersect the pure propane axis at the vapor pressure of propane. Nevertheless, this envelope is too small to be plotted on this figure. The break points on Figure 4 for these two isotherms are the corresponding three-phase point for the aqueous phase.

Because of the excellent results for the propane-water binary, we have confidence in extending the methods to the ternary mixture.

The system water-MDEA-propane

As noted earlier, calculations for the ternary system were done assuming that the aqueous phase was 3 M MDEA on a propane-free basis. For the bubble point calculations, this simply meant that the feed was specified by indicating the amount of propane. The concentrations of the water and the MDEA were calculated using the ratio 12.475 mol H_2O/mol MDEA. A standard algorithm was then used to calculate the bubble point pressure and the vapor composition at a specified temperature. For the LLE and VLLE calculations, a second iteration was required. An arbitrary feed composition was selected. Standard algorithms were used to perform a liquid-liquid flash, a three-phase bubble point or a three-phase dew point calculation (Peng and Robinson, 1976b), depending on the situation under consideration. A check was performed to

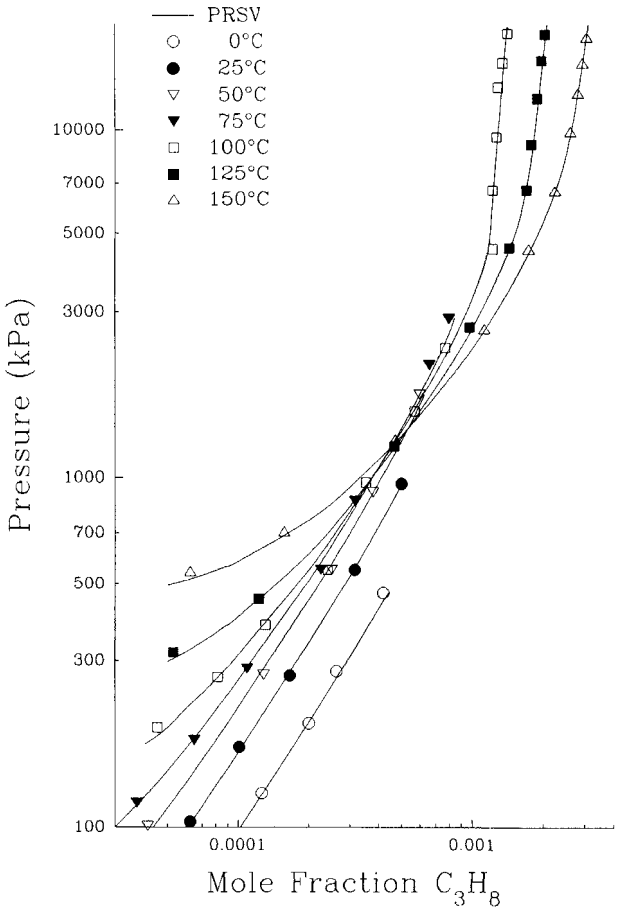

Figure 6. Bubble points for mixtures of propane and 3 M MDEA aqueous solutions.

determine if the aqueous phase was 3 M MDEA on a propane-free basis. If not, the feed composition was adjusted and the calculation repeated. Otherwise the procedure was stopped. In all of the runs performed, there was never a problem arriving

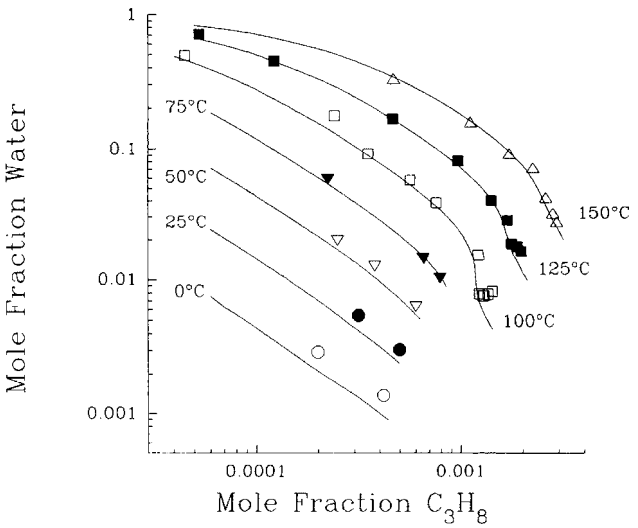

Figure 7. Water content of the vapor for the propane-3 M MDEA system.

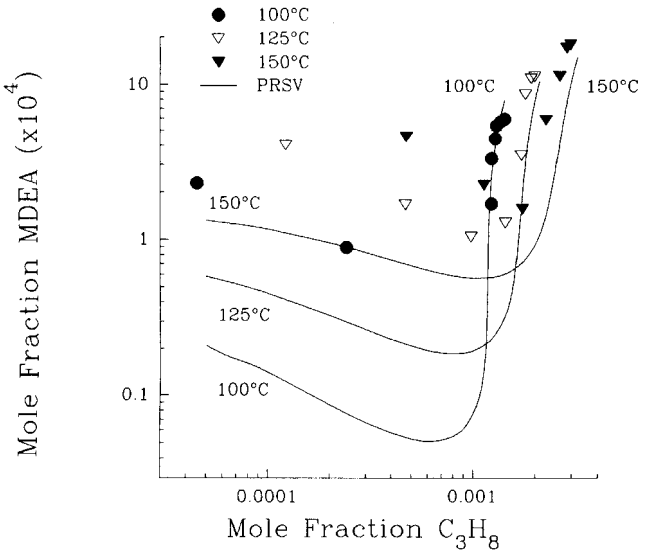

Figure 8. MDEA content of the vapor for three isotherms for the propane-3 M MDEA system.

at a solution after only a few iterations on the feed composition. Thus, the problem of specifying the feed composition for a three-component system was overcome. The suitability of the pseudo-binary approach is discussed later in this paper.

Figure 6 shows the bubble points for the ternary mixture for seven isotherms. For the 0, 25, 50 and 75°C isotherms the curves end at the three-phase dew point. From this figure the three-phase dew points at 0 and 25°C are clear, but those at 50 and 75°C are somewhat hidden. Note that at high pressure the curves become very steep. The steepness causes some computational difficulties. For mixtures lean in propane, the bubble point pressure increases with increasing temperature. For mixtures richer in propane, the reverse is true. The bubble point pressure decreases with increasing pressure. The transition occurs at about $x_{C_3H_8} = 5 \times 10^{-4}$. This is true for both

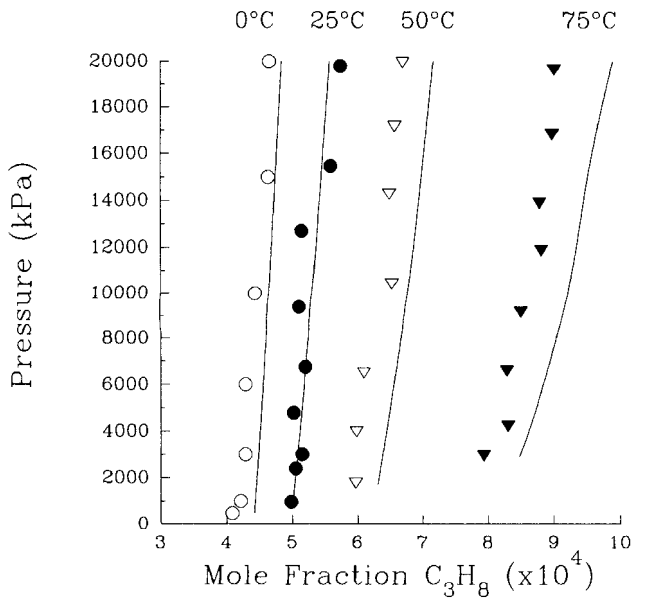

Figure 9. Solubility of liquid propane in 3 M MDEA.

the experimental data and the correlation, as shown in Figure 6. The errors in the calculated bubble points were noted earlier.

The excellent agreement between the experimental and calculated bubble point pressures is not surprising since these values were used to obtain the optimum interaction parameters. However, it is important that there be no systematic deviation between the experiment and the calculation. This plot reveals no such error.

Figure 7 shows the compositions of water content of the vapor in equilibrium with the liquid for which the bubble points were calculated. From this figure, it can be seen that the predicted water content of the vapor agrees well with the experimental values. Somewhat larger deviations occur for the lower temperatures.

Figure 8 shows the MDEA content of the vapor at the bubble point. The mole fraction of MDEA in the vapor for 100, 125 and 150°C has a minimum. For mixtures rich in propane the predicted MDEA concentration is quite good. At lower propane concentrations in the liquid, the predicted MDEA concentration is in error by an order of magnitude. Changing the value of $k_{C_3H_8\text{-MDEA}}$ has the effect of translating these curves. Thus, it is possible to improve the fit for mixtures lean in propane. However, this would dramatically worsen the fit for mixtures rich in propane resulting in unrealistically high estimates of the MDEA concentration. Thus, it was concluded that this type of accuracy was sufficient and $k_{C_3H_8\text{-MDEA}}$ was left equal to zero. The 0, 25, 50 and 75°C isotherms were not included in this figure for clarity. The errors for these isotherms are about the same as those for the temperatures shown. These isotherms do not have the pronounced minimum of the higher temperatures because of the formation of a third phase.

Now, consider the liquid-liquid equilibrium. Since the LLE data were *not* used to obtain the interaction parameters, these calculations represent a true prediction. Figure 9 shows the solubility of liquid propane in the 3 M MDEA solution. From this figure, it can be seen that the prediction is very good. The average absolute error in the estimated solubility is 4.7% and the maximum absolute error is 9.5%. The solubilities begin at the three-phase bubble point and extend to higher pressures. Both the experimental data and the prediction show that the solubility of liquid propane in 3 M MDEA solution is a weak function of pressure (that is, the curves on Figure 9 are very steep).

In the liquid-liquid region, the predicted MDEA and water concentrations in the L_P phase are correct to about the right order of magnitude. At lower pressures, the prediction for the MDEA concentration is in error by an order of magnitude. Its poorest value is at the three-phase bubble point. It may seem logical to attempt to improve this fit by changing $k_{C_3H_8\text{-MDEA}}$, but this was found to provide only a small change in this region and, as noted earlier, leads to worse predictions at other conditions. This reinforced the decision to leave this parameter equal to zero.

Finally, calculations were performed for the liquid-liquid-vapor region. Figure 10 shows the three-phase boundary for the ternary mixture. One drawback to the pseudo-binary approach is that it predicts that the three-phase dew and bubble points are the same. Since the aqueous phase composition is fixed, one degree of freedom is lost. From the experimental data, a small difference between the dew and bubble points was observed. In spite of this, the agreement between the

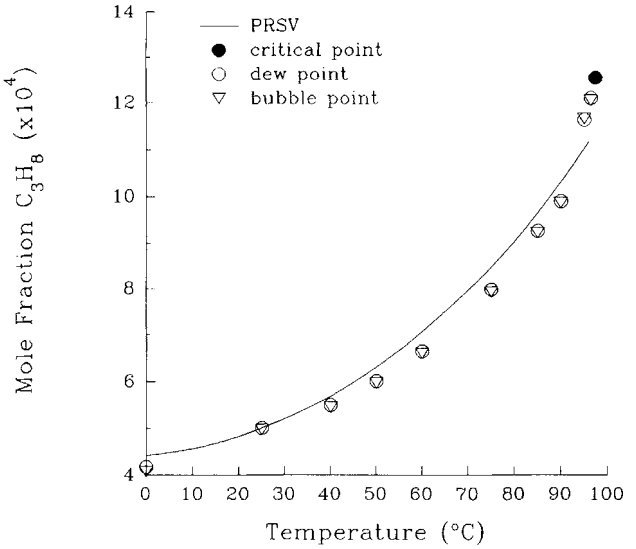

Figure 10. Three-phase region for the propane-3 M MDEA system.

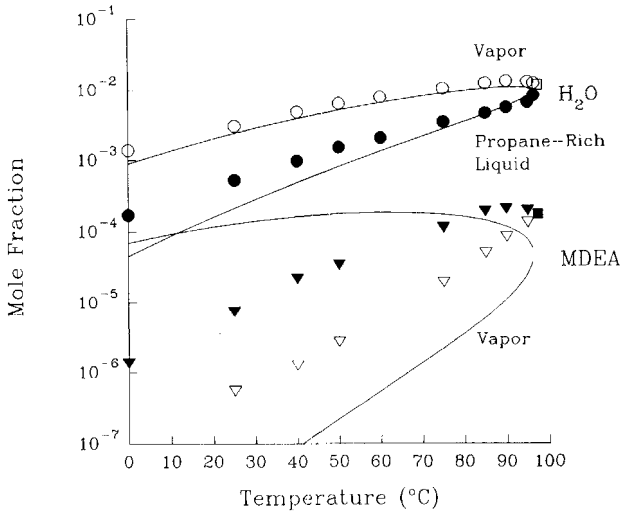

Figure 12. Water and MDEA content of the propane-rich phases in the three-phase region for the propane-3 M MDEA system.

calculation and experiment is very good. The average absolute error in the predicted three-phase dew point pressure is only 1.1% and for the bubble point it is only 3.4%.

The propane content of the aqueous liquid in the three-phase region is shown in Figure 11. As with the LLE calculations, the predicted concentrations of the propane in the aqueous amine solution are in good agreement with the experimental values. The average absolute error is 4.9%. This includes both the dew and bubble point compositions. The concentration of propane in L_A had a minimum for the binary system, as shown in Figure 3. The ternary does not exhibit this minimum.

Figure 12 shows the water and MDEA content of the propane-rich phases in the three-phase region. One point about this figure is somewhat confusing. The concentration of water in the vapor is less than it is in the L_P phase. Thus, for water, the upper curve and data points are for the vapor. On the other hand, there is more MDEA in the L_p phase than in the vapor. Thus, for MDEA, the upper curve and data points are for the L_P phase. The fit of the water content of the propane-rich phases in the three-phase region is quite good. Unfortunately, the fit of the MDEA concentrations is poor. At least the prediction is qualitatively correct. Fortunately, the amount of MDEA in the propane-rich phases is small in both cases. As noted earlier, the MDEA concentration in the L_P is the poorest at the three-phase bubble point.

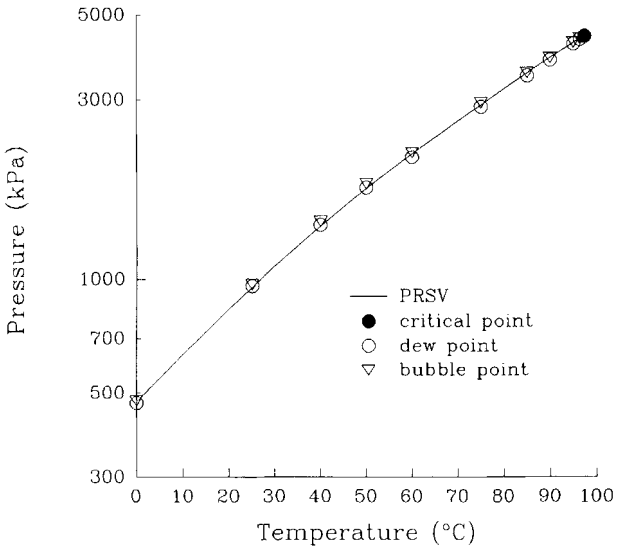

Figure 11. Propane content of the aqueous phase in the three-phase region for the propane-3 M MDEA system.

A comment on the pseudo-binary approach

It is important to note that the calculations were independent of the amount of propane in the feed as long as the aqueous phase was 3 M MDEA on a propane-free basis. As well, small variations from the 3 M assumption did not have a dramatic effect on the calculations either.

Table 5 lists the experimental bubble point at 125°C. Also listed are the calculated bubble points for several different feed compositions. In each case, the propane concentration in the feed was 0.1434 mol %. The first entry in this table is the experimental value. The second is the calculation for a feed that has the proper ratio of water to MDEA (3 M) on a propane-free basis. The remainder of the entries are for feeds that deviate slightly from the ratio 12.475 mol H_2O/mol MDEA. Figure 6 demonstrates that the bubble point is a strong function

Table 5. Effect of Feed Composition on Calculated Bubble Point for a Mixture of Propane, Water and MDEA at 125°C and 0.1434 mol % Propane in the Feed

Feed Composition				L_P Composition	
Mole Frac. Water	Mole Frac. MDEA	Ratio*	Pres. (kPa)	Mole Frac. Water	Mole Frac. MDEA
Experimental			4,550	4.00×10^{-2}	1.28×10^{-4}
0.924,461	0.074,105	12.475	4,474	4.01×10^{-2}	0.33×10^{-4}
0.923,500	0.075,566	12.302	4,349	4.15×10^{-2}	0.32×10^{-4}
0.924,000	0.074,566	12.392	4,413	4.08×10^{-2}	0.32×10^{-4}
0.925,000	0.075,566	12.574	4,548	4.15×10^{-2}	0.33×10^{-4}
0.925,500	0.073,066	12.667	4,619	3.89×10^{-2}	0.34×10^{-4}

*mol H_2O/mol MDEA

Table 6. Effect of Feed Composition on Calculated Liquid-Liquid Flash for a Mixture of Propane, Water and MDEA at 75°C and 9,160 kPa

Feed		Aqueous Phase	Propane-Rich Liquid	
Mole Frac. Propane	Ratio*	Mole Fraction Propane	Mole Fraction Water	Mole Fraction MDEA
Experimental		8.49×10^{-4}	3.06×10^{-3}	1.83×10^{-4}
0.1000	12.475	9.13×10^{-4}	2.06×10^{-3}	3.70×10^{-4}
0.2500	12.475	9.13×10^{-4}	2.06×10^{-3}	3.70×10^{-4}
0.5000	12.475	9.13×10^{-4}	2.06×10^{-3}	3.70×10^{-4}
0.7500	12.475	9.13×10^{-4}	2.06×10^{-3}	3.70×10^{-4}
0.9000	12.475	9.13×10^{-4}	2.06×10^{-3}	3.70×10^{-4}
0.5000	12.000	9.58×10^{-4}	2.04×10^{-3}	4.18×10^{-4}
0.5000	12.250	9.34×10^{-4}	2.05×10^{-3}	3.92×10^{-4}
0.5000	12.750	8.89×10^{-4}	2.07×10^{-3}	3.45×10^{-4}
0.5000	13.000	8.69×10^{-4}	2.08×10^{-3}	3.25×10^{-4}

*mol H_2O/mol MDEA

of the amount of propane in the feed. Thus, variations of the magnitude of those in Table 5 are considered to be reasonable.

In Table 6, the experimental value and the results of the liquid-liquid flash calculation for several feed compositions are listed. The temperature and pressure are 75°C and 9160 kPa for both the experimental value and the calculations. The first entry in the table is the experimental composition of the coexisting liquids. The next five entries are for mixtures that are 3 M MDEA on a propane-free basis; however, each has a different amount of propane in the feed. Note that the calculated phase compositions are independent of the amount of propane in the feed. The final four entries are for mixtures that deviate slightly from the ratio 12.475 mol H_2O/mol MDEA. As can be seen from Table 6, small deviations from 12.475 ratio result in relatively small variations in the calculated compositions.

The seemingly large number of significant figures in Tables 5 and 6 is dictated by the concentration of propane in the feed. As shown in Figure 6, the bubble points are sensitive to the amount of propane in the feed.

The applicability of the pseudo-binary assumption is important from an experimental point of view as well. It is impossible to make a solution that is exactly 3 M. As well, the concentration of the aqueous solution changes slightly due to the transfer of material between the phases. It is anticipated that such a change would be small. The calculations using the PRSV equation indicate that small deviations from 3 M do not have a dramatic effect on the observed phenomena.

Conclusions

New data were obtained for the fluid phase equilibria in the system water-MDEA-propane. The new data were accurately correlated using the Stryjek-Vera modification of Peng-Robinson equation of state using a composition- and temperature-dependent mixing rule. Such information should be useful for the design of processes for stripping acid gas components from LPG.

Acknowledgment

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Notation

a = parameter in PRSV equation of state, kPa·m^6/kmol^2
b = parameter in PRSV equation of state, m^3/kmol
k_{ij} = interaction parameter in modified mixing rule, unitless
K = three-phase critical end point
L_A = aqueous liquid phase
L_P = propane-rich liquid phase
P = pressure, kPa
P_c = critical pressure, kPa
Q = quadruple point
R = gas constant, $R = 8.314$ kPa·m^3/kmol·K
T = absolute temperature, K
T_c = critical temperature, K
T_R = reduced temperature, unitless
V = vapor phase
v = specific volume, m^3/kmol
x_i = mole fraction of component, unitless

Greek letters

α = parameter in PRSV equation of state, unitless
δ_{ij} = interaction parameter in original mixing rule, unitless
κ = parameter in PRSV equation of state, unitless
κ_0 = parameter in PRSV equation of state, unitless
κ_1 = parameter in PRSV equation of state, unitless
ω = acentric factor, unitless

Subscripts

i = component i
j = component j

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