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Liquid–Liquid Equilibria for Mixtures of an Alkanol + Hept-1-ene + Water at 25 °C

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The tie line and liquid–liquid equilibrium data are presented for mixtures of an alkanol + hept-1-ene + water at 25 °C. The data are compared to the related mixtures of an alkanol + heptene + water at 25 °C. The alkanol refers to all the C_1, C_2, C_3, and C_4 alcohols. The measurements have a bearing on the water contamination problem inherent in gasoline + alcohol blends.

In many parts of the world, alkanols are being added to motor fuels to extend fossil fuels. According to Fox and Arthur (*1*), alkanols are also being added to motor fuels to cut pollution and reduce emission of greenhouse gases. The European Commission presently allows 5% ethanol to be added to fossil fuel, and in South Africa 12% by volume "ethanol plus" (a mixture of ethanol, propanol, and higher alcohols) is added to SASOL gasoline. This is equivalent to a mole fraction of alkanol of 0.20.

Unfortunately alkanols are hygroscopic even when dissolved in gasoline. Phase separation is thus possible in motor fuels containing alkanols. This work is part of an investigation to understand the phase separation behavior in these alkanol + gasoline mixtures. Because gasoline is composed of many types of hydrocarbons, Letcher and co-workers (*2–6*) have investigated alkanol + water blends with aliphatic, aromatic, or cyclic hydrocarbons. The work presented here relates to the hydrocarbon hept-1-ene and is particularly relevant to South Africa and any country using Fischer–Tropsch synthesis to produce gasoline, because such gasoline (called SASOL gasoline in South Africa) contains a high proportion of olefinic compounds.

The tie lines and binodal curve data for mixtures of an alkanol + hept-1-ene + water have been determined at 25 °C for all the C_1, C_2, C_3, and C_4 alkanols. The data have been compared with alkanol–water systems containing heptane. The effect of the type of alkanol on the tie lines and the solubilizing effect on water were also noted. The binodal curve data have been summarized using a Hlavatý-type equation (*7*), a β function, and a log γ function using methods recently described by Letcher (*3*).

Experimental Section

The experimental details have been described by Letcher and Siswana (*6*). The hept-1-ene was supplied by Aldrich and was purified by distillation. Its purity was determined by gas–liquid chromatography and found to be better than 99.8 mol %. The density of the hept-1-ene was found to be 0.692 65 g·cm^{-3}.

The refractive index method reported by Briggs and Comings (*8*) was supported in all cases by a density method using an Anton-Paar DNA 601 vibrating-tube density meter. The density method is similar to the refractive index method, the only difference being that density measurements replaced refractive index measurements.

Table 1. Compositions of Points on the Binodal Curve at 25 °C for the Mixtures $C_mH_{2m+1}OH$ (1) + 1-C_7H_{14}

x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
CH_3OH		C_2H_5OH		C_3H_7OH		$CH_3CH(OH)CH_3$	
0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
0.264	0.731	0.202	0.770	0.080	0.901	0.184	0.773
0.454	0.539	0.361	0.579	0.168	0.792	0.281	0.632
0.601	0.390	0.455	0.457	0.287	0.622	0.365	0.468
0.707	0.283	0.538	0.342	0.365	0.479	0.407	0.330
0.772	0.210	0.596	0.248	0.416	0.343	0.417	0.227
0.805	0.165	0.628	0.171	0.439	0.230	0.402	0.145
0.834	0.102	0.637	0.113	0.433	0.154	0.378	0.084
0.827	0.053	0.611	0.063	0.400	0.090	0.349	0.050
0.750	0.020	0.513	0.022	0.316	0.040	0.273	0.021
0.554	0.012	0.412	0.013	0.248	0.021	0.242	0.011
0.396	0.010	0.300	0.010	0.186	0.010	0.059	0.005
0.239	0.006	0.239	0.005	0.123	0.005	0.027	0.001
0.049	0.001	0.047	0.001	0.026	0.001	0.000	0.000
0.000	0.000	0.000	0.000	0.000	0.000		
C_4H_9OH		$CH_3CH(OH)$-CH_2CH_3		$CH(CH_3)_2$-CH_2OH		$C(CH_3)_3OH$	
0.000	1.000	0.000	1.000	0.000	1.000	0.000	1.000
0.142	0.834	0.142	0.828	0.134	0.848	0.151	0.820
0.259	0.683	0.255	0.683	0.235	0.725	0.255	0.688
0.354	0.546	0.391	0.489	0.365	0.565	0.346	0.563
0.432	0.426	0.430	0.426	0.450	0.440	0.403	0.421
0.491	0.317	0.485	0.323	0.492	0.372	0.437	0.283
0.527	0.231	0.520	0.231	0.519	0.326	0.430	0.200
0.545	0.150	0.521	0.147	0.540	0.285	0.401	0.122
0.549	0.091	0.498	0.082	0.560	0.239	0.345	0.061
0.532	0.038	0.452	0.037	0.576	0.201	0.299	0.040
0.485	0.000	0.322	0.000	0.587	0.162	0.219	0.021
0.019	0.000	0.054	0.000	0.596	0.121	0.189	0.012
0.010	0.001	0.023	0.001	0.599	0.106	0.152	0.009
0.000		0.000	0.000	0.594	0.071	0.109	0.003
				0.584	0.043	0.079	0.001
				0.548	0.000	0.000	0.000
				0.021	0.000		
				0.000	0.000		

[a] x_1 is the mole fraction of component 1, and x_2 is the mole fraction of component 2.

Results

The compositions of mixtures on the binodal curve at 25 °C are given in Table 1, and tie line compositions are given in Table 2. These compositions are plotted in Figure 1. Three

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Table 2. Compositions of the Conjugate Solutions x_1', x_2'', x_1', and x_2'' for $C_mH_{2m+1}OH$ (1) + 1-C_7H_{14} (2) + H_2O (3) at 25 °C

water-rich		heptene-rich		water-rich		heptene-rich	
x_1'	x_2'	x_1''	x_2''	x_1'	x_2'	x_1''	x_2''
CH_3OH				C_2H_5OH			
0.690	0.301	0.375	0.618	0.595	0.246	0.365	0.578
0.805	0.165	0.240	0.754	0.627	0.175	0.330	0.620
0.757	0.020	0.184	0.811	0.639	0.121	0.262	0.700
0.571	0.017	0.116	0.881	0.555	0.033	0.228	0.743
				0.442	0.017	0.193	0.783
				0.239	0.005	0.099	0.890
C_3H_7OH				$CH_3CH(OH)CH_3$			
0.150	0.010	0.365	0.060	0.412	0.270	0.390	0.595
0.134	0.009	0.420	0.128	0.412	0.185	0.372	0.450
0.112	0.008	0.420	0.326	0.382	0.092	0.342	0.518
0.075	0.005	0.349	0.511	0.300	0.032	0.291	0.616
0.026	0.002	0.132	0.838	0.197	0.009	0.190	0.764
C_4H_9OH				$CH_3CH(OH)CH_2CH_3$			
0.015	0.000	0.543	0.168	0.042	0.000	0.527	0.183
0.009	0.001	0.396	0.487	0.027	0.001	0.400	0.478
0.004	0.000	0.190	0.780	0.011	0.000	0.170	0.785
$CH(CH_3)_2CH_2OH$				$C(CH_3)_3OH$			
0.018	0.000	0.595	0.111	0.032	0.001	0.275	0.033
0.015	0.000	0.549	0.271	0.045	0.001	0.355	0.070
0.010	0.000	0.424	0.480	0.055	0.002	0.398	0.116
				0.074	0.003	0.437	0.241
				0.105	0.004	0.409	0.422
				0.135	0.005	0.345	0.565

equations have been fitted to the data following the work of Hlavatý (*7*). The coefficients A_i relate to a modified Hlavatý equation,

$$x_1 = A_1 x_A \ln x_A + A_2 x_B \ln x_B + A_3 x_{AxB} \quad (1)$$

the coefficients B_i relate to a β function equation,

$$x_1 = B_1(1 - x_A)^{B2} x_A^{B3} \quad (2)$$

and the coefficients C_i relate to a log γ equation,

$$x_1 = C_1(-\ln x_A)^{C2} x_A^{C3} \quad (3)$$

where

$$x_A = (x_2 + {}^1/_2 x_1 - x_2°)/(x_{22}° - x_{22}°) \quad (4)$$

$$x_B = (x_{22}° - x_2 - {}^1/_2 x_1)/(x_{22}° - x_2°) \quad (5)$$

and x_1 refers to the mole fraction composition of the alkanol, x_2 refers to the mole fraction of the hept-1-ene and $x_{22}°$ and $x_2°$ are the values of x_2 on the binodal curve which cuts the $x_1 = 0$ axis and have been used to summerize the binodal curve data. These equations have been discussed by Letcher and co-workers (*5*). The coefficients A_i, B_i, and C_i are given in Table 3.

Discussion

No phase equilibrium results have been published in the literature on the mixtures presented here.

The double bond in hept-1-ene has a small positive effect on the mutual solubility of alkanols (especially methanol and ethanol) in hept-1-ene + water mixtures. This can be seen by comparing these measurements with the measurements for the mixtures of an alkanol + heptane + water presented by Letcher and co-workers (*2*). For example, an equilibrium mixture of methanol + heptane + water at 25 °C on the binodal curve containing 0.1 mole fraction heptane will contain 0.005 mole fraction water. A corresponding mixture of methanol + hept-1-ene + water containing 0.1 mole fraction hept-1-ene will contain 0.065 mole fraction water. Similarly an equilibrium mixture of ethanol + heptane + water containing 0.1 mole fraction heptane will contain 0.21 mole fraction water whereas the equilibrium mixture of ethanol + hept-1-ene + water containing 0.1 mole fraction hept-1-ene will contain 0.27 mole fraction water. The effect of the double bond on the ternary mixtures containing the other six alkanols is less marked.

The relative solubility of each alkanol in water or in hept-2-ene is evident from the tie line compositions. The slopes of the tie lines presented here (see Figure 1a,b) indicate that both methanol and ethanol are more soluble in water than in hept-1-ene. The horizontal tie lines for the propan-2-ol mixture (Figure 1c) indicate that propan-2-ol is equally soluble in hept-1-ene and in water. The other five alkanols show a much greater affinity for hept-1-ene than for water (Figure 1d–h).

One of the serious drawbacks of alkanol-blended fuels is the hygroscopic nature of the alkanol and possible corrosion resulting from the inclusion of water and the subsequent phase separation. The corrosion potential is almost certainly a function of the amount of water in the water-rich layer. The higher the water content the higher will be the corrosive nature of the blend. The tie line compositions of Figure 1 can be used to determine this amount of the water in the water-rich layers. In an attempt to compare the alkanols, the water composition in the water-rich layer resulting from adding just enough water to cause phase separation has been calculated for a hept-1-ene + alkanol mixture containing 0.20 mole fraction alkanol before the addition of water. The composition of 0.20 mole fraction was chosen because it approximates the composition of "ethanol plus" added to gasoline in South Africa. The measurements are given in Table 4. The measurements show that alkanol blends involving alkanols other than methanol, ethanol, or propan-2-ol will result in almost pure water separating out when just enough water is added to the blend to cause phase separation. This result is similar to that found for other alkanol + hydrocarbon + water blends where the hydrocarbon is heptane, benzene, cyclohexane, and methyl-substituted benzenes. The phase diagram and tie lines for these systems have been determined by Letcher and co-workers (*2–6*). As these and related hydrocarbons are the major components of gasoline, our conclusions developed here apply equally to gasoline.

The partitioning of the alkanol between the water-rich and the hept-1-ene-rich layers for five of the systems is illustrated

Table 3. Coefficients A_i, B_i, and C_i in Eqs 1–3, Respectively, for $C_mH_{2m+1}OH$ (1) + 1-C_7H_{14} (2) + H_2O (3) at 25 °C[a]

$C_mH_{2m+1}OH$	A_1	A_2	A_3	B_1	B_2	B_3	C_1	C_2	C_3
CH_3OH	1.816	1.860 (0.083)	8.304	4.434	1.295 (0.056)	1.251	3.53	1.174 (0.076)	1.620
C_2H_5OH	0.571	1.188 (0.033)	4.911	3.293	1.299 (0.032	1.147	2.626	1.184 (0.036)	1.521
C_3H_7OH	−0.220	0.203 (0.016)	1.732	0.944	1.117 (0.021)	0.995	1.601	1.039 (0.011)	1.320
$CH_3CH(OH)CH_3$	−0.406	0.030 (0.010)	1.169	1.974	1.142 (0.035)	1.007	1.577	1.030 (0.030)	1.318
C_4H_9OH	−0.902	0.276 (0.008)	1.244	2.849	1.277 (0.038)	1.096	2.242	1.171 (0.047)	1.431
$CH_3CH(OH)CH_2CH_3$	−0.210	0.533 (0.091)	2.510	2.634	1.254 (0.046)	1.073	2.110	1.152 (0.017)	1.424
$CH(OH_3)_2CH_2OH$	−0.998	0.291 (0.005)	1.311	2.932	1.253 (0.028)	1.073	2.381	1.165 (0.027)	1.421
$C(CH_3)_3OH$	−0.175	0.043 (0.006)	11.589	1.787	1.042 (0.010)	0.957	1.535	0.972 (0.009)	1.285

[a] The standard deviations σ are given in parentheses.

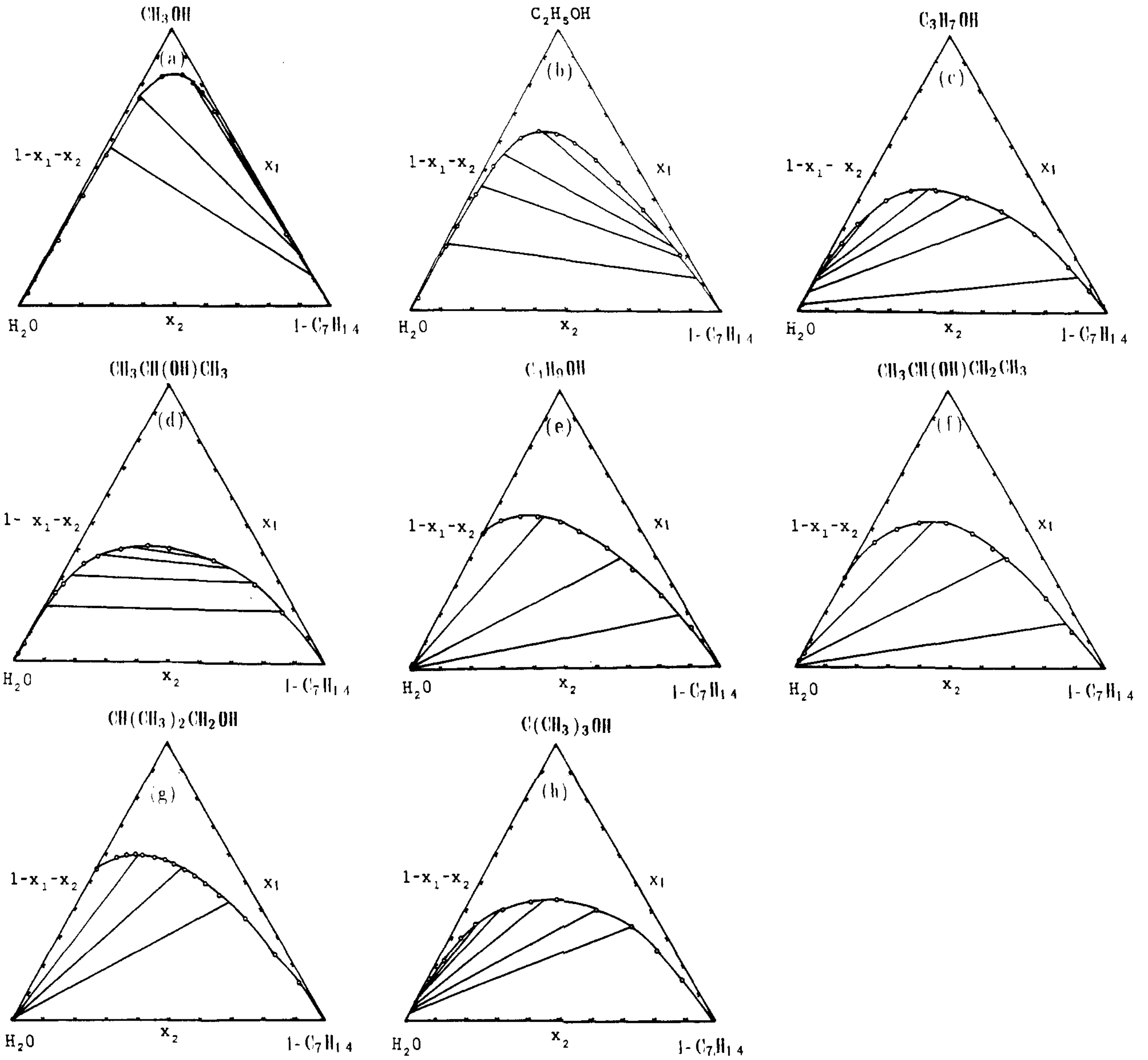

Figure 1. Binodal curves and tie lines for $C_mH_{2m+1}OH$ + 1-C_7H_{14} (2) + H_2O (3) at 25 °C: (a) CH_3OH; (b) C_2H_5OH; (c) C_3H_7OH; (d) $CH_3CH(OH)CH_3$; (e) C_4H_9OH; (f) $CH_3CH(OH)CH_2CH_3$; (g) $CH(CH_3)_2CH_2OH$; (h) $C(CH_3)_3OH$. x_1 and x_2 are mole fractions.

Table 4. Water Composition $(1 - x_1 - x_2)'$ of the Water-Rich Layer Formed by Adding a Minimum Amount of Water to an Alkanol + Hept-1-ene Mixture Containing 0.20 Mole Fraction Alkanol before Water Addition

alkanol	$(1 - x_1 - x_2)'$	alkanol	$(1 - x_1 - x_2)'$
CH_3OH	0.19	C_4H_9OH	0.99
C_2H_5OH	0.51	$CH_3CH(OH)CH_2CH_3$	0.99
C_3H_7OH	0.95	$CH(CH_3)_2CH_2OH$	0.99
$CH_3CH(OH)CH_3$	0.78	$C(CH_3)_3OH$	0.99

in Figure 2, where the mole fraction of each alkanol in the conjugate layers has been plotted. The estimated plait points are indicated in Figure 2 with dotted lines crossing the 45° line and by filled circles in Figure 1.

Equations 1–3 have been discussed previously and have been fitted to the binodal curve data in Table 1. Good fits were obtained for each of the equations. The results, given in Table 3, include the standard deviations σ. This is defined as

$$\sigma = [\sum [x_1(\text{calcd}) - x_1(\text{exptl})]^2/(n - 3)]^{1/2} \qquad (6)$$

where n is the number of data points and 3 is the number of estimated coefficients (9).

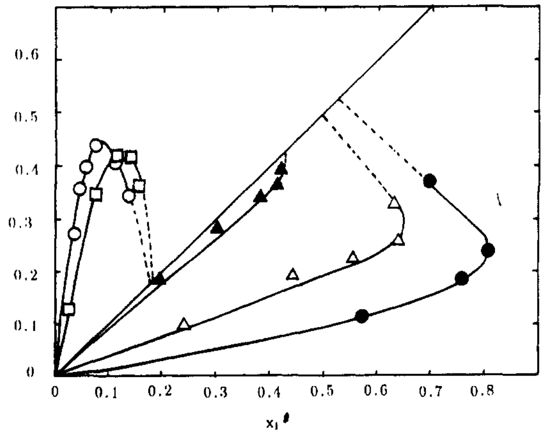

Figure 2. A plot of x_1' and x_1'' from Table 2 showing the relative solubility of the alcohol in the water-rich and hept-1-ene-rich layers: ●, CH_3OH; △, C_2H_5OH; □, C_3H_7OH, ▲, $CH_3CH(OH)CH_3$; ○, $C(CH_3)_3OH$.

In conclusion our measurements show that an olefinic double bond does have a small positive enhancement effect on the solubility of water in alkanol + water + hept-1-ene mixtures. If water solubility is an important property in alkanol fuel blends, then olefins will improve the situation.

Furthermore, our results show that when hept-1-ene is mixed with propan-1-ol or C_3 or C_4 alkanols and contaminated with just enough water to cause phase separation, then the water-rich layer contains over 0.95 mole fraction water. A similar conclusion can be made for gasoline blends containing these alkanols.

Literature Cited

(1) Fox, B.; Arthur, C. *New Sci.* **1992**, Oct 24, 21.
(2) Letcher, T. M.; Wooten, S.; Shuttleworth, B.; Heyward, C. *J. Chem. Thermodyn.* **1986**, *18*, 1037.
(3) Letcher, T. M.; Sewry, J. D.; Radloff, S. *S. Afr. J. Chem.* **1990**, *43*, 56.
(4) Letcher, T. M.; Sizwana, P.; Radloff, S. *S. Afr. J. Chem.* **1991**, *44*, 118.
(5) Letcher, T. M.; Ravindran, S.; Radloff, S. *Fluid Phase Equilibr.* **1992**, *71*, 177.
(6) Letcher, T. M.; Sizwana, P. M. *Fluid Phase Equilib.* **1992**, *74*, 203.
(7) Hlavatý, K. *Collect. Czech. Chem. Commun.* **1972**, *37*, 4005.
(8) Briggs, S. W.; Comings, E. W. *Ind. Eng. Chem.* **1943**, *35*, 411.
(9) Mendenhal, W.; Wackerly, D. D.; Schaefer, R. L. *Mathematical Statistics with Applications*, P.W.S. Kent: Boston, 1990; p 515.

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