Articles

Vapor−Liquid Equilibrium of Binary Mixtures. 1. Ethanol + 1-Butanol, Ethanol + Octane, 1-Butanol + Octane

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The activity coefficients of the binary mixtures ethanol + 1-butanol, ethanol + octane, and 1-butanol + octane were determined at temperatures of (308.15, 313.15, and 318.15) K. The determination of the vapor phase composition at equilibrium was carried out using headspace gas chromatography analysis. Multiple headspace extraction was used to calibrate the headspace gas chromatograph. Comparison of the phase diagrams produced using standard Legendre orthogonal polynomial techniques with phase diagrams from the literature showed good agreement. The composition of the azeotropes were reported, where applicable.

Introduction

There is considerable interest in using oxygen-containing compounds, including those of biological origin, as fuel additives. Apart from improving the anti-knock properties of gasoline, they can also be useful as alternative fuel components. In addition, biologically sourced additives generally reduce the net carbon dioxide emissions to the atmosphere from the combustion of hydrocarbons.

One of the drawbacks of adding components such as alcohols to gasoline is a possible increase in the vapor pressure of the fuel. This is a well-known effect in the case of adding ethanol to gasoline. An increase in the vapor pressure of the fuel increases among other things its flammability, not a desirable consequence. To analyze the effects produced by adding oxygenates to the fuel, basic knowledge is required about the phase equilibrium of multicomponent mixtures containing these compounds.

The study of gasoline + alcohol mixtures using the methods of physical−chemical analysis is considered at the present time as a difficult goal as gasoline is an extremely complex mixture of hydrocarbons of varying composition. Accordingly, a more appropriate approach would seem to be to study model hydrocarbon + alcohol mixtures composed of a small number of individual compounds.

The goal of this study was to use gas chromatography to measure the concentrations of the components of binary mixtures of alcohols and hydrocarbons in the vapor phase. The concentration data was obtained at the vapor−liquid equilibrium (VLE) of various binary mixtures including ethanol + 1-butanol, ethanol + octane, and 1-butanol + octane at temperatures of (308.15, 313.15, and 318.15) K. From the concentration data, various thermodynamic quantities can be calculated such as the activity, activity coefficient, vapor pressure, and Gibbs energy of mixing.

The experimental data were compared with that available in the literature for binary mixtures.[1−5] Sufficient similarity of the two sets of data confirms the suitability of using the method of headspace gas chromatography for studying the VLE of binary mixtures comprising alcohols and hydrocarbons.

Experimental Section

Materials. The reagents 1-butanol and octane with a main substance content of not lower than 99.8 % by volume were obtained from Merck. Ethanol 99.7 % by volume was obtained from Solveco Chemicals AB. All these reagents were used without additional purification. In addition, chromatographic analysis of the reagents did not reveal any admixtures.

Equipment. The equipment used consisted of a headspace sampler and a gas chromatograph equipped with a flame ionization detector. The laboratory was a temperature- and humidity-controlled facility at atmospheric pressure.

The headspace sampler was a Perkin-Elmer HS-40 automatic headspace sampler.[6] It uses the pneumatic balanced pressure technique with a defined sample volume. The full sample stream was used with no split sampling. VLE was obtained in 20 mL standard vials, filled with a constant amount of fluid mixture, closed with polytetrafluoroethylene-coated, aluminum crimped seals. The sampling technique proceeded in three successive steps: thermostating, pressurization, and injection. The vial was thermostated at a constant temperature with a tolerance of ± 0.1 K until equilibrium was reached. The time required for equilibrium was several hours, depending on the specific sample composition, and was determined experimentally in advance. Once equilibrium was reached, the vial was pressurized to the column head pressure of 85 kPa with the carrier gas, helium in this case. The carrier gas flow was then directed to the column while stopping the flow to the vial, constituting the injection

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step. Except for the specialized technique of multiple headspace extraction (see the Methods section), only a single extraction was made from each vial.

The gas chromatograph was a Perkin-Elmer Autosystem XL GC temperature-programmable gas chromatograph. The detection of the compounds present in the carrier gas flow was obtained with a flame ionization detector. The carrier gas is mixed with hydrogen and burned in air, generating ions. The ions are collected and measured with a concentration proportional to the amount of compound present.[7] The area of the concentration measured as a function of time is calculated automatically using standard routines supplied with the equipment. Only measurements with clearly defined areas were accepted.

The column used was a Varian XCOT fused silica 25 m × 0.32 mm i.d. coating CP-SIL CB low bleed/MS df = 1.20. The gases used in the analysis were helium of detector quality in a 20 L cylinder, hydrogen of detector quality in a 20 L cylinder, and synthetic air of instrument quality in a 50 L cylinder, all placed in the laboratory. The cylinders were used from full down to only 20 % capacity to ensure a stable head pressure. The liquid mole fractions of the samples were determined using standard laboratory weighing techniques.

Methods. Two GC methods were used to obtain the activities of binary mixtures: multiple headspace extraction (MHE) and standard headspace extraction.[8] MHE provides a technique for the calibration of a gas chromatograph. The basic idea is to carry out a succession of analyses of samples from the same headspace vial. The corresponding peak areas are obtained in the usual way. Unlike the normal headspace operation, there is only a single phase in the vial, namely, the gas phase. This requires the introduction of a small amount of sample into the vial, 1 μL for a 20 mL vial, so that it completely evaporates. The result of the analysis gives the response factor of the gas chromatograph to a known amount of moles of substance.

The headspace equipment used was equipped with a pneumatic balanced pressure mechanism, as opposed to a syringe extraction. Once the sample is extracted, the vial is allowed to vent to the atmosphere. In this way a portion of the sample is deliberately lost. The cycle is then repeated. The technique is similar to exponential dilution.

The procedure for calculating the calibration of the instrument follows that of Kolb and Ettre.[8] Since the loss of substance from the vial is proportional to the amount of substance in the vial, the ratio between successive peak areas A_{i+1}/A_i is a constant Q:

$$\frac{A_{i+1}}{A_i} = Q < 1 \tag{1}$$

The constant Q can be determined from the experimental data. The sample exits the vial, so $Q < 1$.

Results of MHE experiments are shown in Figure 1 for a three-component mixture ethanol + 1-butanol + octane. The data are plotted as a semilog plot, that is log A_n against the extraction number n. A straight line fit can be achieved to a high accuracy, with a standard deviation of 0.0002 or lower. The first area is subject to the greatest error, so the analysis is best characterized in terms of the slope of the fitted line and its y-intercept. The initial amount of substance s is proportional to the total peak area obtained by carrying out MHE to exhaustion:

$$s = F \sum_{1}^{\infty} A_i \tag{2}$$

where F is a constant.

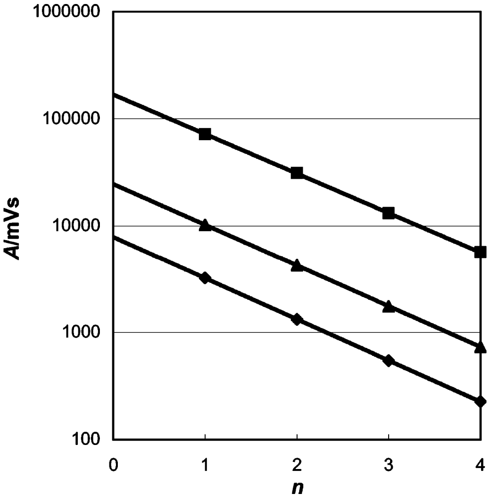

Figure 1. Plot of multiple headspace extraction data where the peak area A is shown in terms of the extraction number n. The lines are least-squares linear approximations to the data; ■, octane; ▲, 1-butanol; ◆, ethanol.

Table 1. Summary of Calibration Factors f from Equation 4 and Standard Deviation of the Calibration Factor σ

species	f/mol·area^{-1}	σ/mol·area^{-1}
1-butanol	4.56×10^{-10}	5.7×10^{-12}
ethanol	9.84×10^{-10}	1.1×10^{-11}
octane	2.15×10^{-10}	2.9×10^{-12}
2,2,4-trimethylpentane	1.96×10^{-10}	3.1×10^{-12}
o-xylene	3.52×10^{-10}	5.6×10^{-12}

From eq 1 all the areas can be written in terms of the first one $A_i = A_1Q^{i-1}$. This is the basis of the sampling technique in that the first extraction is a determining characteristic of the contents of the vial. Equation 2 is rearranged as

$$s = FA_1 \sum_{1}^{\infty} Q^{i-1} = FA_1 \sum_{0}^{\infty} Q^{i} = \frac{FA_1}{1 - Q} = fA_1 \quad |Q| < 1 \tag{3}$$

where the response factor $f = F/(1 - Q)$ relates the amount of substance in the vial to the first peak area. Equation 3 shows that the total amount of substance in the vial is proportional to the first peak area. It is not necessary to perform the MHE cycle ad infinitum; just sufficient extractions to be able to estimate Q adequately.

The response factor f relates specifically to a given substance. It is readily obtained from the y-intercept of the graph of the data fit as in Figure 1. Designating the y-intercept of the fitted line as A_0, eq 3 obtains using eq 1

$$f = \frac{s}{A_1} = \frac{s}{QA_0} \tag{4}$$

where log Q is the gradient of the line.

Table 1 contains a summary of the calibration factors, where for convenience the factors for components appearing in the accompanying paper[16] are listed. The standard deviations are small indicating the low degree of uncertainty associated with this type of measurement. The uncertainty ranges from 1.2 % for ethanol to 1.6 % for o-xylene. The amount of substance in the vapor phase n_i is calculated directly from the peak areas using the calibration factors as

$$n_i = f_iA_i \tag{5}$$

The procedure for using standard headspace extraction gas chromatography for the determination of the activity coefficients

Table 2. Experimental Data for the Mixture Ethanol (1) + 1-Butanol (2), Liquid Mole Fraction x, Vapor Mole Fraction y, and Activity Coefficient γ at Temperature T, Standard Deviation σ Using Equation 10, and Point Test Consistency ϵ

x_1	y_1	γ_1	γ_2	x_1	y_1	γ_1	γ_2
T/K = 308.15, $\sigma = 0.030$, $\epsilon = 0.001$							
0.0307	0.1936	0.989	1.000	0.6344	0.9303	0.998	0.995
0.0607	0.3289	0.990	1.000	0.6691	0.9396	0.999	0.995
0.0912	0.4323	0.990	1.000	0.7067	0.9489	0.999	0.994
0.1076	0.4779	0.991	1.000	0.7397	0.9563	0.999	0.994
0.1502	0.5732	0.992	1.000	0.7701	0.9627	0.999	0.993
0.1769	0.6204	0.992	1.000	0.7971	0.9681	1.000	0.993
0.2063	0.6642	0.993	1.000	0.8319	0.9745	1.000	0.992
0.2327	0.6978	0.993	0.999	0.8629	0.9799	1.000	0.991
0.2858	0.7531	0.994	0.999	0.8925	0.9847	1.000	0.991
0.3315	0.7910	0.995	0.999	0.9204	0.9889	1.000	0.990
0.3838	0.8264	0.996	0.998	0.9296	0.9903	1.000	0.990
0.4283	0.8514	0.996	0.998	0.9464	0.9927	1.000	0.990
0.4691	0.8712	0.997	0.997	0.9584	0.9944	1.000	0.989
0.5134	0.8900	0.997	0.997	0.9690	0.9959	1.000	0.989
0.5568	0.9060	0.998	0.996	0.9843	0.9979	1.000	0.989
0.5937	0.9182	0.998	0.996				
T/K = 313.15, $\sigma = 0.030$, $\epsilon = 0.001$							
0.0307	0.1774	0.949	1.000	0.6344	0.9267	0.993	0.978
0.0607	0.3062	0.952	1.000	0.6691	0.9366	0.994	0.975
0.0912	0.4075	0.955	1.000	0.7067	0.9465	0.995	0.972
0.1076	0.4529	0.956	0.999	0.7397	0.9544	0.996	0.970
0.1502	0.5494	0.960	0.999	0.7701	0.9612	0.997	0.967
0.1769	0.5979	0.963	0.998	0.7971	0.9668	0.998	0.965
0.2063	0.6434	0.965	0.998	0.8319	0.9736	0.998	0.962
0.2327	0.6786	0.968	0.997	0.8629	0.9792	0.999	0.959
0.2858	0.7370	0.972	0.995	0.8925	0.9842	0.999	0.956
0.3315	0.7773	0.975	0.994	0.9204	0.9886	1.000	0.954
0.3838	0.8152	0.979	0.992	0.9296	0.9900	1.000	0.953
0.4283	0.8421	0.982	0.990	0.9464	0.9925	1.000	0.951
0.4691	0.8633	0.984	0.988	0.9584	0.9943	1.000	0.950
0.5134	0.8835	0.987	0.985	0.9690	0.9958	1.000	0.949
0.5568	0.9007	0.989	0.983	0.9843	0.9979	1.000	0.947
0.5937	0.9137	0.991	0.980				
T/K = 318.15, $\sigma = 0.030$, $\epsilon = 0.001$							
0.0307	0.1724	0.974	1.000	0.6344	0.9219	0.996	0.989
0.0607	0.2986	0.976	1.000	0.6691	0.9323	0.997	0.988
0.0912	0.3984	0.978	1.000	0.7067	0.9427	0.998	0.986
0.1076	0.4434	0.978	1.000	0.7397	0.9511	0.998	0.985
0.1502	0.5392	0.980	0.999	0.7701	0.9582	0.999	0.984
0.1769	0.5876	0.982	0.999	0.7971	0.9642	0.999	0.983
0.2063	0.6332	0.983	0.999	0.8319	0.9714	0.999	0.981
0.2327	0.6686	0.984	0.999	0.8629	0.9774	0.999	0.980
0.2858	0.7275	0.986	0.998	0.8925	0.9828	1.000	0.978
0.3315	0.7683	0.988	0.997	0.9204	0.9876	1.000	0.977
0.3838	0.8068	0.990	0.996	0.9296	0.9892	1.000	0.977
0.4283	0.8343	0.991	0.995	0.9464	0.9919	1.000	0.976
0.4691	0.8562	0.992	0.994	0.9584	0.9938	1.000	0.975
0.5134	0.8769	0.994	0.993	0.9690	0.9954	1.000	0.975
0.5568	0.8948	0.995	0.992	0.9843	0.9977	1.000	0.974
0.5937	0.9084	0.995	0.990	0.9952	0.9993	1.000	0.973

of binary mixtures is summarized in Kolb and Ettre[8] and in Pettersson et al.[9] The system consists of two fluid components distributed in a gas and a liquid phase. The system is at equilibrium so the pressure and temperature are constant for the whole system. The liquid phase is further characterized by two mole fractions x_1 and x_2 corresponding to the two components. The gas phase is similarly characterized by the two mole fractions y_1 and y_2.

The mole fraction of each component in the vapor phase of a binary mixture is calculated as

$$y_1 = \frac{n_1}{n_1 + n_2} = \frac{f_1A_1}{f_1A_1 + f_2A_2} = \left(1 + \frac{f_2A_2}{f_1A_1}\right)^{-1}$$

$$y_2 = \frac{n_2}{n_1 + n_2} = \left(1 + \frac{f_1A_1}{f_2A_2}\right)^{-1} \qquad (6)$$

Table 3. Experimental Data for the Mixture Ethanol (1) + Octane (2), Liquid Mole Fraction x, Vapor Mole Fraction y, and Activity Coefficient γ at Temperature T, Standard Deviation σ Using Equation 10, and Point Test Consistency ϵ

x_1	y_1	γ_1	γ_2	x_1	y_1	γ_1	γ_2
T/K = 308.15, $\sigma = 0.038$, $\epsilon = 0.0078$							
0.055	0.713	9.397	0.938	0.656	0.806	1.251	2.458
0.106	0.755	6.515	1.073	0.687	0.812	1.269	2.759
0.153	0.771	4.666	1.074	0.722	0.822	1.241	2.999
0.197	0.777	3.759	1.138	0.750	0.821	1.260	3.524
0.238	0.780	3.041	1.151	0.778	0.828	1.210	3.770
0.309	0.791	2.491	1.266	0.816	0.836	1.141	4.252
0.348	0.814	2.494	1.306	0.853	0.839	1.026	4.883
0.411	0.816	2.173	1.465	0.879	0.849	1.019	5.616
0.471	0.820	1.924	1.612	0.910	0.868	1.023	6.709
0.523	0.806	1.632	1.852	0.955	0.908	1.038	9.548
0.569	0.811	1.436	1.889	0.969	0.928	1.014	10.515
0.611	0.814	1.347	2.077	0.988	0.967	1.011	11.833
T/K = 313.15, $\sigma = 0.052$, $\epsilon = 0.0011$							
0.055	0.693	8.975	0.993	0.656	0.821	1.442	2.585
0.106	0.763	6.405	1.020	0.687	0.819	1.437	3.023
0.153	0.774	4.674	1.063	0.722	0.821	1.326	3.232
0.197	0.781	4.106	1.225	0.777	0.828	1.151	3.594
0.238	0.802	3.661	1.221	0.853	0.848	1.091	4.931
0.309	0.783	2.583	1.387	0.901	0.866	1.098	6.714
0.348	0.786	2.356	1.476	0.919	0.879	1.068	7.144
0.441	0.798	2.025	1.753	0.959	0.918	1.051	9.519
0.523	0.810	1.702	1.892	0.969	0.933	1.012	9.583
0.569	0.811	1.627	2.162	0.980	0.952	1.001	10.483
0.611	0.808	1.559	2.511	0.996	0.988	1.000	12.008
T/K = 318.15, $\sigma = 0.033$, $\epsilon = 0.0022$							
0.055	0.683	8.840	1.035	0.687	0.818	1.379	2.939
0.106	0.754	6.115	1.034	0.722	0.822	1.230	3.004
0.153	0.774	4.731	1.088	0.750	0.826	1.169	3.231
0.197	0.784	3.948	1.164	0.778	0.829	1.127	3.538
0.238	0.789	3.366	1.225	0.816	0.839	1.049	3.906
0.309	0.796	2.536	1.271	0.866	0.854	1.007	4.842
0.348	0.799	2.389	1.394	0.901	0.867	1.003	6.100
0.411	0.800	1.950	1.484	0.943	0.901	1.001	7.903
0.471	0.800	1.865	1.815	0.969	0.935	1.019	9.543
0.523	0.803	1.667	1.953	0.971	0.938	1.001	9.588
0.569	0.805	1.509	2.102	0.979	0.951	0.988	10.207
0.611	0.812	1.383	2.189	0.996	0.988	1.001	12.212
0.656	0.817	1.380	2.567				

The activity coefficients γ_i of the components of a binary mixture are given from the equilibrium of Gibbs energy at the vapor−liquid interface in the vial as[10]

$$P_i = y_iP = x_i\gamma_iP_i^0 \qquad (7)$$

where P_i is the partial pressure of component i, P is the vapor pressure, P_i^0 is the vapor pressure of the pure component i. From Mohliner et al.,[11] using eq 5 and the ideal gas equation the activity coefficients are given in terms of the peak area of the sample mixture A_i and the pure components A_i^0 as

$$\gamma_i = \frac{P_i}{x_iP_i^0} = \frac{A_i}{x_iA_i^0} = \frac{a_i}{x_i} \qquad (8)$$

where a_i is the activity of component i. The pure component peak area is

$$A_i^0 = \frac{P_i^0\nu}{f_iRT} \qquad (9)$$

where ν is the volume of the sample, R is the molar gas constant, and T is the temperature.

Results. Tables 2 to 4 contain the experimental data for the binary mixtures ethanol + 1-butanol, ethanol + octane, and 1-butanol + octane at temperatures of (308.15, 313.15, and

Table 4. Experimental Data for the Mixture 1-Butanol (1) + Octane (2), Liquid Mole Fraction x, Vapor Mole Fraction y, and Activity Coefficient γ at Temperature T, Standard Deviation σ Using Equation 10, and Point Test Consistency ϵ

x_1	y_1	γ_1	γ_2	x_1	y_1	γ_1	γ_2
T/K = 308.15, σ = 0.047, ϵ = 0.0022							
0.038	0.165	8.531	0.962	0.552	0.324	1.233	1.772
0.070	0.210	6.401	1.019	0.601	0.356	1.286	1.958
0.104	0.226	4.758	1.055	0.663	0.378	1.249	2.266
0.133	0.259	4.589	1.131	0.701	0.385	1.158	2.423
0.168	0.252	3.473	1.164	0.733	0.387	1.110	2.696
0.217	0.271	2.794	1.165	0.769	0.413	1.109	2.930
0.265	0.284	2.610	1.326	0.824	0.463	1.089	3.309
0.311	0.293	2.345	1.429	0.876	0.506	1.061	4.105
0.366	0.299	1.930	1.456	0.917	0.594	1.009	4.288
0.416	0.306	1.798	1.620	0.970	0.773	1.020	5.402
0.464	0.316	1.631	1.707	0.991	0.917	0.964	5.605
0.508	0.329	1.555	1.826				
T/K = 313.15, σ = 0.044, ϵ = 0.0022							
0.070	0.241	7.204	1.029	0.552	0.354	1.419	1.915
0.104	0.249	4.736	1.001	0.601	0.370	1.326	2.047
0.133	0.262	4.224	1.104	0.663	0.395	1.208	2.188
0.168	0.289	3.678	1.098	0.701	0.406	1.159	2.396
0.208	0.301	3.173	1.167	0.753	0.439	1.092	2.564
0.226	0.301	2.761	1.126	0.796	0.477	1.091	2.819
0.265	0.311	2.528	1.214	0.824	0.501	1.046	2.928
0.311	0.317	2.068	1.210	0.876	0.540	1.038	3.775
0.366	0.325	1.938	1.395	0.910	0.617	0.995	3.751
0.416	0.334	1.615	1.383	0.958	0.748	0.947	4.399
0.464	0.347	1.663	1.628	0.991	0.930	0.936	4.902
0.508	0.359	1.560	1.726				
T/K = 318.15, σ = 0.040, ϵ = 0.0022							
0.038	0.184	8.751	0.999	0.508	0.377	1.483	1.631
0.104	0.269	4.965	1.009	0.552	0.379	1.360	1.770
0.133	0.286	4.263	1.058	0.601	0.395	1.345	1.999
0.168	0.291	3.622	1.149	0.663	0.423	1.322	2.286
0.208	0.300	2.882	1.140	0.701	0.434	1.227	2.423
0.226	0.307	2.699	1.146	0.733	0.454	1.100	2.347
0.265	0.322	2.577	1.261	0.783	0.481	1.087	2.727
0.311	0.331	2.357	1.387	0.876	0.560	0.990	3.556
0.366	0.345	1.880	1.328	0.910	0.636	1.055	3.926
0.416	0.347	1.718	1.484	0.946	0.718	0.990	4.363
0.464	0.364	1.642	1.604	0.980	0.860	0.988	4.995

318.15) K. The liquid mole fraction x_1 of the first component was obtained from the known composition of the sample. The vapor mole fraction y_1 was obtained using eq 6. The activity coefficients of both components, γ_1 and γ_2, were obtained using eq 8.

Tables 2 to 4 contain experimental data necessary for the calculation of the activity and other physical chemical parameters of the mixtures studied. The standard deviations σ reported were calculated according to the formula

$$\sigma = \left\{\frac{1}{N}\sum_{i=1}^{2}\sum_{j=1}^{N}(\ln \gamma_{ij} - \ln \gamma_i(x_j))^2\right\}^{1/2} \tag{10}$$

where γ_{ij} is the activity coefficient of component i for data point j and $\ln \gamma_i(x_j)$ is the natural logarithm of the value of an activity coefficient fitting function and N is the number of sample points. More details of the functions used and the smoothing procedures are contained in the Phase Diagrams section of this paper and the Verification Tests section of the accompanying paper.[16] The details of the point test and the point test consistency parameter are also given in ref 16.

Discussion

Comparison of Results with Existing Literature Data. The most readily accessible approach to comparing the experimental with the literature data is by using the vapor pressure. The vapor pressure is the sum of the partial pressures of each component, which from eq 7 is

Table 5. Comparison of Experimental Data with Literature Values for Mixture Ethanol (1) + Octane (2), EO, and 1-Butanol (1) + Octane (2), BO[a]

	T	σ	x_1		
	K	kPa	(e)	(l)	ref
EO	313.15	0.084	0.835	0.835	3
EO	318.15	0.265	0.852	0.835	2
BO	308.15	0.036	0.298	0.282	3
BO	313.15	0.047	0.310	na	3
BO	318.15	0.050	0.329	na	3

[a] Standard deviation is defined as $\sigma = 1/N(\sum \Delta P^2)^{1/2}$. Azeotrope composition x_1 is given for experimental data (e) and literature data (l), which is indicated with the corresponding reference. na, not available.

$$P = \sum_{i=1}^{2} P_i = \sum_{i=1}^{2} x_i \gamma_i P_i^0 \tag{11}$$

Direct use of the vapor pressure calculated from experimental values does not easily allow a comparison with literature data as the data points do not generally coincide at values of the independent variable, the mole fraction of component 1, x_1. The procedure adopted here was to fit the experimental data to a suitable model, giving a function on the whole domain of $x_1 \in [0, 1]$. The deviation of the experimental data from the literature data was then calculated as the distance of the literature data from the experimental data fit.

A suitable model is one without bias on the domain. Standard activity models such as Wilson, UNIQUAC, and NRTL do not have this property as they are designed to model certain observed physical chemical behavior. The techniques introduced by Gmehling and Onken,[12] van Ness et al.,[13] and Fredenslund et al.[14] based on using the convergence properties of orthogonal series, in this case Legendre orthogonal polynomials, avoid this difficulty. Following Gmehling and Onken,[12] the experimental data are fitted to a Legendre series of the form

$$g^e = \frac{\Delta G^e}{RT} = x_1(1 - x_1)\sum_{i=0}^{n} a_i L_i(2x_1 - 1) \tag{12}$$

where L_i are Legendre polynomials and a_i are constant coefficients of the series.

Two additional results for the activity coefficients are required to be able to calculate the vapor pressure from eq 11:[12]

$$\ln \gamma_1 = g^e + (1 - x_1)\frac{dg^e}{dx_1} \tag{13}$$

$$\ln \gamma_2 = g^e - x_1\frac{dg^e}{dx_1} \tag{14}$$

The vapor pressure is given by the final result:[12]

$$P = x_1 P_1^{\,0} \exp\left(g^e + x_2\frac{dg^e}{dx_1}\right) + x_2 P_2^{\,0} \exp\left(g^e - x_1\frac{dg^e}{dx_1}\right) \tag{15}$$

where $x_1 + x_2 = 1$.

The results for three comparisons with literature data are shown in Table 5. The values of P_i^0, the vapor pressure of the pure component i, were obtained from the online NIST database.[15] The table gives the standard deviation of the distance

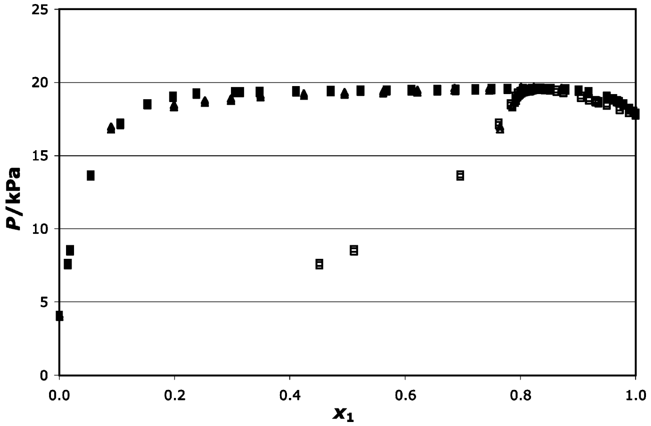

Figure 2. Phase diagram of the mixture ethanol (1) + octane (2) T/K = 313.15 with ■, bubble point; ▲, bubble point from literature; □, dew point; △, dew point from the literature (3).

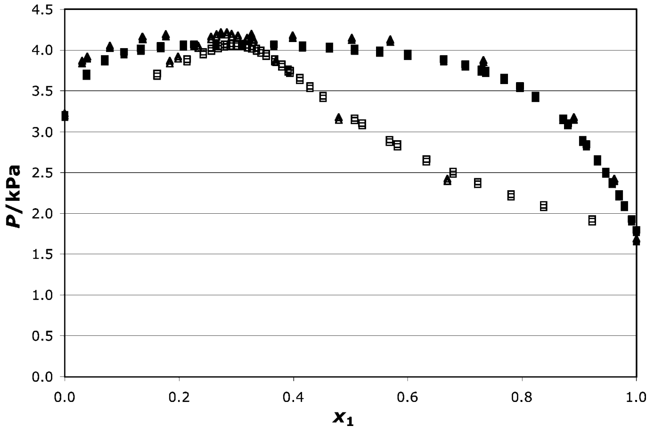

Figure 3. Phase diagram of the mixture 1-butanol (1) + octane (2) T/K = 308.15 with ■, bubble point; ▲, bubble point from literature; □, dew point; △, dew point from the literature (3).

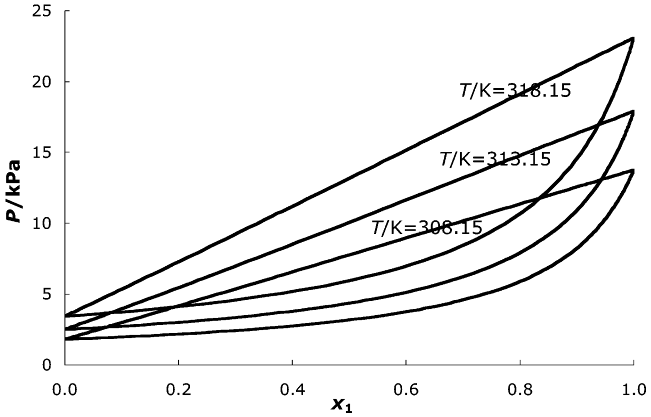

Figure 4. Phase diagram of the mixture ethanol (1) + 1-butanol (2) for the temperatures as indicated. At each temperature there is a pair of curves; the upper one being the bubble point curve and the lower one being the dew point curve.

to the literature data in terms of the pressure difference between the two sets of data. Also shown in the table is a comparison of estimates of the azeotropes for each mixture. The agreement is good for all the mixtures shown.

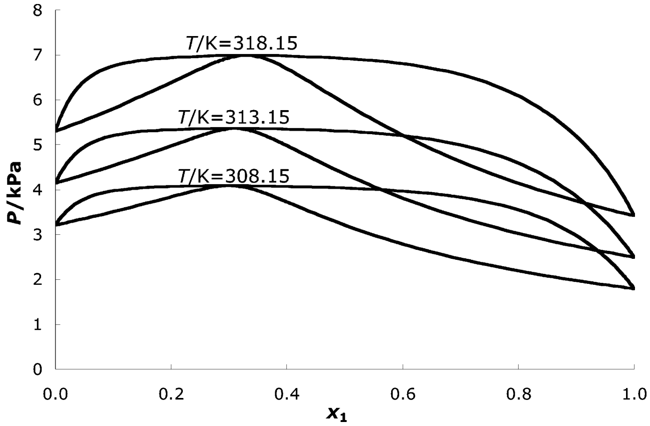

Figure 5. Phase diagram of the mixture 1-butanol (1) + octane (2) for the temperatures as indicated. At each temperature there is a pair of curves; the upper one being the bubble point curve and the lower one being the dew point curve. Azeotropes are given in Table 6.

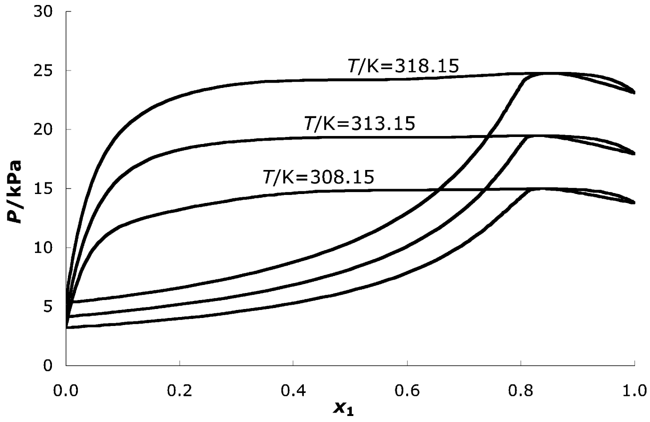

Figure 6. Phase diagram of the mixture ethanol (1) + octane (2) for the temperatures as indicated. At each temperature there is a pair of curves; the upper one being the bubble point curve and the lower one being the dew point curve. Azeotropes are given in Table 6.

Table 6. Azeotrope Compositions x_1 at Temperature T of the Mixtures Studied

T/K	x_1
Ethanol (1) + Octane (2)	
308.15	0.838
313.15	0.835
318.15	0.852
1-Butanol (1) + Octane (2)	
308.15	0.298
313.15	0.310
318.15	0.329

Figures 2 and 3 compare the phase diagrams for the mixtures ethanol + octane and 1-butanol + octane obtained from refs 1−5 and those based on the experimental data obtained in the present study. Figures 2 and 3 and the results of Table 5 demonstrate that the phase diagrams for the known mixtures 1-butanol + octane and ethanol + octane and the corresponding diagrams calculated from the experimental data for these mixtures are similar. This allows the use of the method of gas−liquid chromatography for studying VLE of the binary mixtures comprising alcohols and hydrocarbons and the use of the Legendre polynomial averaging procedure for calculating physical parameters of such mixtures.

Considerable possibilities of the GC analysis method for studying the mixtures with low concentrations of one of the components should also be noted. The experimental data obtained complement the literature data for the mixtures 1-butanol + octane and ethanol + octane.

Phase Diagrams. The complete phase diagrams of the mixtures in this study are shown in Figures 4 to 6. The data shown are smoothed data using eq 15 so that the diagrams can be shown as curves rather than individual data points. The smoothing was carried out with the use of the technique discussed in the section and in eq 7 and eqs 11 to 14. The compositions of the azeotropes have been calculated by determining the point of intersection of the bubble and dew curves shown in Figures 5 and 6. The results are shown in Table 6. For both the mixtures ethanol + octane and 1-butanol + octane, the azeotrope increases slightly with temperature; that is, it occurs at higher concentrations of the alcohol. Calculation of the infinite dilution values of the activity coefficient are reported in the accompanying paper.[16]

Conclusions

A comparative analysis of the experimental results of the VLE of two component mixtures obtained from headspace GC and literature data available for the same mixtures shows the possibility of investigating VLE using headspace GC.

The activity coefficients of the binary mixtures ethanol + 1-butanol, ethanol + octane, and 1-butanol + octane at temperatures of (308.15, 313.15, and 318.15) K have been studied using the method of headspace GC analysis.

The vapor pressure of the binary mixtures ethanol + 1-butanol, ethanol + octane, and 1-butanol + octane at temperatures of (308.15, 313.15, and 318.15) K have been calculated using the experimentally obtained activity coefficients. Diagrams of the vapor−liquid phase equilibrium of the binary mixtures ethanol + 1-butanol, ethanol + octane, and 1-butanol + octane at temperatures of (308.15, 313.15, and 318.15) K have been plotted using Legendre polynomial approximations for the data smoothing.

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