Glossary

F	flow rate of carrier gas
GLC	gas–liquid chromatography
$\bar{h}_i^{E\infty}$	partial molar excess enthalpy at infinite dilution
m_{CS}	mass of solid support
m_{ein}	mass of coated solid support
m_k	mass of strongly adsorbed water
m_{stat}	mass of stationary phase
M_L	molecular weight of solvent
P_a	pressure at column outlet
P_e	pressure at column inlet
P_{fm}	pressure at soap bubble flowmeter
P_i^s	saturation vapor pressure of solute (solvent)
P_W	saturation vapor pressure of water
R	gas constant
T	absolute temperature
t_a	dead time
t_R	retention time
T_{fm}	temperature at soap bubble flowmeter
VLE	vapor–liquid equilibrium
V_g^0	specific net retention volume corrected to 0 °C
X	liquid loading
X_k	liquid loading with strongly adsorbed water ($X_k = m_k/m_{CS}$)
γ_i^∞	activity coefficient of component i at infinite dilution
φ_i^s	solute fugacity coefficient of component i in saturated state

Registry No. NFM, 4394-85-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; isooctane, 540-84-1; 1-hexene, 592-41-6; methanol, 67-56-1; ethanol, 64-17-5; ethyl acetate, 141-78-6; *n*-propyl acetate, 109-60-4; diethyl ether, 60-29-7; acetone, 67-64-1; methyl ethyl ketone, 78-93-3; cyclohexane, 110-82-7; methylcyclopentane, 96-37-7; butanal, 123-72-8; benzene, 71-43-2; toluene, 108-88-3; dichloromethane, 75-09-2; 1,1,2-trichlorotrifluoroethane, 76-13-1; 10-nonadecanone, 504-57-4; 1-pentanol, 71-41-0; *m*-xylene, 108-38-3.

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Vapor–Liquid Equilibrium Measurements for Methyl Propanoate–Ethanol and Methyl Propanoate–Propan-1-ol at 101.32 kPa

Pedro Susial and Juan Ortega*

Cátedra de Termodinâmica y Fisicoquimica, Escuela Superior de Ingenieros Industriales, Polytechnic University of Canarias, 35017 Las Palmas, Canary Islands, Spain

Casiano de Alfonso and Carlos Alonso

Unidad de Tribologia e Ingenieria Quimica, Instituto Rocasolano, CSIC, Madrid, Spain

Isobaric vapor–liquid equilibrium measurements on binary systems of methyl propanoate with ethanol and propan-1-ol are taken at a constant pressure of 101.32 ± 0.02 kPa. These systems exhibit significant deviations from ideality and are shown to be thermodynamically consistent. The methyl propanoate–ethanol system forms an azeotrope at $x = y = 0.483$ and $T = 345.58$ K. Experimental data are fitted to a suitable equation and are likewise compared with the values predicted by the UNIFAC and ASOG models.

Introduction

Experimental vapor–liquid equilibrium information is of great assistance in studying and understanding liquid mixtures. Moreover, experimental data, particularly those of VLE, are very important in thermodynamics in the designing of industrial separation processes. As a continuation of the experimental studies carried out in our laboratory of mixtures of esters and alkanols (*1*–*3*), we report here on the isobaric vapor–liquid equilibrium data at 101.32 ± 0.02 kPa of two systems formed by methyl propanoate with ethanol and propan-1-ol. The vapor–liquid equilibria for the system methyl propanoate–ethanol have previously been studied (*4*) under isothermal conditions of 298.15 K. No experimental isobaric data of either of the systems studied here appear in the literature, but data of the azeotrope for the system $x\,H_5C_2COOCH_3 + (1 - x)C_2H_5(OH)$ at $x = y = 0.515$ and $T = 345.15$ K are reported in ref *5*.

In this article, the results will be treated thermodynamically, considering the nonideality of both phases, verifying their

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Table I. Comparison of the Properties of Pure Liquids Determined in This Work at 298.15 K and 101.32 kPa with Their Corresponding Literature Values[a]

substance	ρ/kg m^{-3}	n_D	NBP/K
methyl propanoate	908.53	1.3740	351.65
	909.0 (*6*)	1.3742 (*6*)	352.52 (*9*)
	908.9 (*4*)		
ethanol	785.01	1.3594	351.46
	784.93 (*7*)	1.35941 (*7*)	351.443 (*7*)
	785.09 (*8*)	1.35941 (*8*)	351.49 (*8*)
propan-1-ol	799.65	1.3835	370.10
	799.60 (*6*)	1.38370 (*6*)	370.301 (*6*)
	799.75 (*8*)	1.3837 (*8*)	370.35 (*8*)

[a] Reference numbers in parentheses.

thermodynamic consistency by means of the classical methods described in the relevant literature.

The idea of obtaining equilibrium properties has been slightly modified at present, such that, without abandoning experimental determination, indispensable in many cases, the tendency is to predict equilibrium data by using generalized methods that permit the calculation of the properties of the mixtures. Among these methods, the most noteworthy are those of group contribution, mainly those of UNIFAC and ASOG. Thus, in this work and with the parameters extracted from the literature, the corresponding predictions were carried out with both methods, the results being compared with the experimental data.

Experimental Section

Chemicals. Both the methyl propanoate and the 1-alkanols were supplied by Fluka and used without further purification. The characteristics indicated by the manufacturer for each of the products were methyl propanoate, purum > 99 mol %, ethanol, puriss p.a. > 99.8 mol %, and propan-1-ol, puriss p.a. > 99.5 mol %. However, prior to use they were degassed with ultrasound and dried with a molecular sieve, type A4, by Fluka.

In order to characterize these products, three physical properties were determined, the values obtained compared with the data reported in the literature; the said properties were density (ρ), the refraction index (n_D), and the normal boiling point (NBP). The results are summarized in Table I, the good concordance between our data and those found in the literature for 1-alkanols being observed; the same does not occur with methyl propanoate, which shows a difference of almost 1 K in its NBP.

Apparatus and Procedure. In order to achieve the equilibrium data, the system described in ref *1* was used, with slight modifications in the coolant so as to promote a better circulation of the vapor phase. Likewise, and with regard to the above-mentioned equipment, changes were made in the pressurization system and in the apparatus for measuring the temperature.

In order to better control the pressure, two electronic systems were placed in series. The first, from Fisher (VKH100), was the system with which the "gross" adjustment was performed and the second, from Normschliff Gerateban Wertheim, was the system used for making a "fine" adjustment of the pressure selected. By means of the corresponding electronically controlled valves, these apparatus correct the variations of the pressure existing between the equilibrium still and the working pressure, the latter being indicated in an electronic systems by MKS Instruments with a probe permitting readings of ±0.001 kPa. The accuracy of the variations of pressure is, in any case, better than ±0.02 kPa. In order to measure the temperature of equilibrium, a Comark (6800) digital thermometer was used, with a platinum probe and giving a reading of ±0.01 K, which was previously calibrated in accordance with IPS-68 regulations, and whose mean error was estimated to be 0.01% of the reading.

The compositions of the vapor and liquid phases were obtained by densimetry, using a vibrating-tube densimeter by Anton Paar (DMA 60/602), calibrated according to the technique described by Ortega et al. (*10*). Before measurement of the concentrations of the samples in equilibrium, the densities of a series of mixtures of known composition were determined at 298.15 ± 0.01 K, the uniform distribution of the v^E for both systems being verified from these data. However, since the v^E are indirectly determined from the densities, the compositions were calculated from the $\rho = \rho(x)$ correlations with an accuracy of ±0.0005 unit in the determination of the liquid mole fractions, x, and ±0.001 in those of vapor, a correction being taken into account in the latter due to possible evaporation.

Results and Discussion

The vapor-liquid equilibrium data at 101.32 ± 0.02 kPa obtained in the direct experimentation are given in Table II together with the liquid-phase activity coefficients determined for each equilibrium state by means of eq 1 (see ref *11*):

$$\ln \gamma_i = \ln(y_i p/x_i p^\circ_i) + [(B_{ii} - v^L_i)(p - p^\circ_i) + p(1 - y_i)^2\delta_{ij}]/RT \qquad (1)$$

where δ_{ij} is related to the second virial coefficients by

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \qquad (2)$$

The second virial coefficients were determined by the correlation of Pitzer and Curl (*12*) with the modification introduced by Tsonopoulos (*13*). In order to determine the second virial cross-coefficients, B_{ij}, the rules of mixing given in ref *11* were used. The calculation of the critical temperature of mixing, $T_{c_{ij}}$, was made by way of the correction of the geometric mean value of the critical temperatures of the pure compounds, that is

$$T_{c_{ij}} = (1 - k_{ij})(T_{c_i}T_{c_j})^{1/2} \qquad (3)$$

A value of 0.14 was used for k_{ij}, as recommended by Tarakad and Danner (*14*) for mixtures with alkanols. The vapor pressures, p°_i, were calculated by means of the Antoine equation, using the constants extracted from ref *7* and *9* for the alkanols and methyl propanoate, respectively. The molar volume data, v^L_i, for eq 1, of the pure compounds were estimated by means of a modified version of the Rackett equation (*15*). The activity coefficients reported in Table II show that the systems studied present a significant deviation from the ideal solution behavior.

The thermodynamic consistency of the data obtained was carried out with three of the most widely used methods: the areas method (*16*) and that of Herington (*17*) to analyze the overall consistency of the data and the point-to-point method proposed by Fredenslund et al. (*18*). The two systems studied here proved to be consistent in every case, presenting deviations below the limits established by the authors of each test.

The prediction of the vapor compositions was also performed for these systems from the T-x data, utilizing the UNIFAC and ASOG models. In both cases, the values of y were determined by using eq 1 and with the procedure described above. In order to compare the results obtained, a correlation of concentration data, x-y, was carried out, with the following polynomial function (*19*):

$$y - x = x(1 - x)\sum A_i\,[x/\{x + k(1 - x)\}]^i \qquad i = 0, 1, 2, 3, \ldots \qquad (4)$$

the corresponding coefficients for each systems are the following: for methyl propanoate-ethanol, $A_0 = 1.189$, $A_1 = -3.853$, $A_2 = 4.210$, $A_3 = -2.666$, $k = 1.01$, and $s(y - x) = 0.0014$; for methyl propanoate-propan-1-ol, $A_0 = 2.134$, $A_1 = -2.886$, $A_2 = 1.560$, $A_3 = -0.718$, $k = 0.422$, and $s(y -$

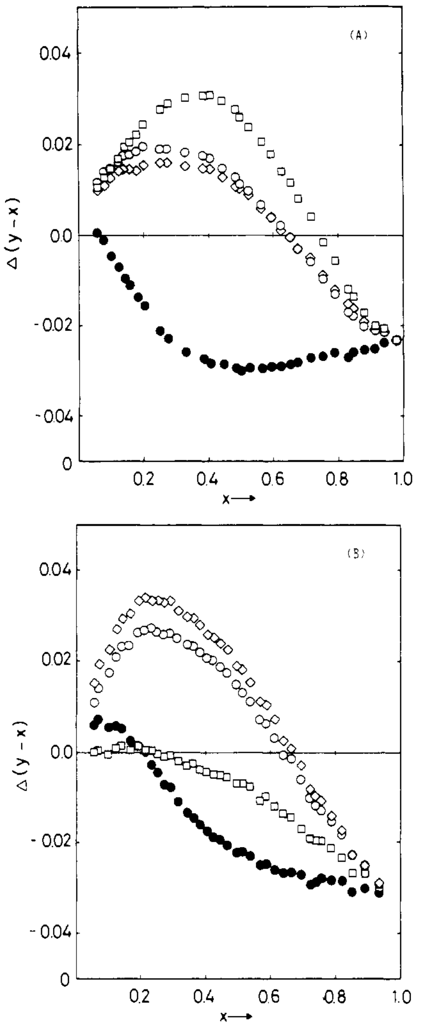

Figure 1. Representation of differences indicated by eq 5 using ASOG and UNIFAC models for (A) methyl propanoate–ethanol and (B) methyl propanoate–propan-1-ol. The curves fitted to experimental points are over the x axis. (●) ASOG; (□) UNIFAC with the pair COOC/CCOH; (◇) UNIFAC with the pair COO/COH; (O) UNIFAC with the pair COOC/OH.

Table II. Experimental Data of Vapor–Liquid Equilibrium for Methyl Propanoate–Alkan-1-ol at 101.32 ± 0.02 kPa

T/K	x_1	y_1	γ_1	γ_2
Methyl Propanoate (1)–Ethanol (2)				
349.75	0.0576	0.1092	2.061	1.008
349.25	0.0784	0.1429	2.013	1.012
348.75	0.0982	0.1740	1.989	1.016
348.35	0.1199	0.2033	1.928	1.019
348.05	0.1383	0.2263	1.878	1.023
347.75	0.1557	0.2458	1.830	1.030
347.45	0.1754	0.2683	1.791	1.035
347.25	0.1965	0.2891	1.734	1.040
346.65	0.2492	0.3333	1.607	1.068
346.45	0.2727	0.3536	1.568	1.077
346.05	0.3282	0.3909	1.460	1.116
345.80	0.3823	0.4246	1.372	1.158
345.75	0.4035	0.4402	1.350	1.169
345.65	0.4402	0.4625	1.305	1.201
345.58	0.4814	0.4861	1.257	1.243
345.55	0.4924	0.4892	1.238	1.263
345.55	0.5230	0.5117	1.219	1.285
345.55	0.5603	0.5326	1.185	1.334
345.65	0.5922	0.5532	1.161	1.370
345.75	0.6231	0.5731	1.139	1.410
345.85	0.6510	0.5902	1.119	1.456
345.95	0.6721	0.6047	1.107	1.489
346.25	0.7140	0.6385	1.090	1.542
346.55	0.7517	0.6667	1.071	1.618
346.95	0.7881	0.6974	1.055	1.695
347.45	0.8280	0.7384	1.046	1.770
347.75	0.8440	0.7551	1.039	1.810
348.35	0.8767	0.7957	1.035	1.861
349.15	0.9116	0.8446	1.030	1.914
349.95	0.9398	0.8895	1.026	1.937
351.15	0.9789	0.9586	1.022	1.977
Methyl Propanoate (1)–Propan-1-ol (2)				
367.05	0.0572	0.1556	1.776	1.010
366.45	0.0716	0.1841	1.707	1.014
364.95	0.1010	0.2497	1.712	1.019
364.15	0.1258	0.2875	1.618	1.026
363.55	0.1425	0.3125	1.580	1.032
362.65	0.1657	0.3544	1.581	1.031
361.85	0.1933	0.3921	1.534	1.036
361.25	0.2138	0.4137	1.489	1.049
360.65	0.2350	0.4408	1.469	1.053
360.15	0.2532	0.4612	1.448	1.060
359.65	0.2713	0.4806	1.429	1.068
359.25	0.2909	0.4983	1.398	1.077
358.65	0.3146	0.5216	1.377	1.088
358.10	0.3413	0.5442	1.346	1.102
357.75	0.3616	0.5596	1.320	1.114
357.35	0.3820	0.5749	1.299	1.129
356.95	0.4044	0.5919	1.279	1.143
356.65	0.4238	0.6055	1.260	1.156
356.35	0.4453	0.6210	1.241	1.168
356.05	0.4651	0.6331	1.222	1.186
355.60	0.4948	0.6550	1.205	1.203
355.35	0.5142	0.6666	1.189	1.221
355.05	0.5381	0.6807	1.170	1.245
354.65	0.5659	0.6975	1.154	1.276
354.45	0.5892	0.7123	1.139	1.293
354.15	0.6134	0.7267	1.127	1.321
353.85	0.6391	0.7420	1.114	1.352
353.65	0.6647	0.7569	1.100	1.383
353.35	0.6941	0.7759	1.089	1.415
353.05	0.7226	0.7927	1.079	1.461
352.95	0.7405	0.8038	1.071	1.484
352.85	0.7571	0.8151	1.066	1.501
352.65	0.7880	0.8343	1.054	1.554
352.45	0.8193	0.8557	1.047	1.601
352.20	0.8522	0.8798	1.043	1.647
352.05	0.8906	0.9084	1.035	1.706
351.85	0.9341	0.9444	1.032	1.734

x) = 0.0016. Figure 1 displays graphically the deviations presented by both predictive methods, the difference being situated on the ordinate axes.

$$\Delta(y - x) = (y - x)_{\text{estd by ASOG or UNIFAC}} - (y - x)_{\text{calcd by eq 4}} \qquad (5)$$

The parameters taken for the ASOG method were those reported by Kojima and Tochigi (*20*), considering the CH_2, OH, and COO groups in both binary systems. The prediction of the vapor concentrations, y, performed with this model, presented a mean deviation from the experimental values of 4.5% for the system methyl propanoate–ethanol and of 2.7% for the system methyl propanoate–propan-1-ol.

The prediction with the UNIFAC model was made considering different cases, upon taking into account that the alkanols intervening in the mixtures might be formed by different functional groups. In the first case, the alkanols include the group in the "COH" form, taking into account, moreover, the CH_3, CH_2, and COO groups, with the interaction parameters taken from Fredenslund et al. (*21*). The prediction carried out of the vapor compositions produces a mean deviation of 0.013 for methyl propanoate–ethanol and of 0.021 for methyl propanoate–propan-1-ol, with mean errors of 3.4 and 4.5%, respectively. When the "OH" group is considered in the alkanol and, in addition, the CH_3, CH_2, and COOC groups and the parameters reported by Kjold-Jorgensen et al. (*22*) are considered, the UNIFAC model prediction causes mean deviations in y of 0.014 (mean error of 3.9%) for methyl propanoate–ethanol and 0.018 (mean error of 3.6%) for methyl propanoate–propan-1-ol. In the third and last case, taking into account the "CCOH" functional group, the presence of the CH_3 and COOC groups, and the interaction parameters given in ref *18*, a mean estimation of the vapor concentrations is obtained of 0.019 (mean error of 5.1%) for methyl propanoate–ethanol and of 0.009 (mean error of 1.4%) for methyl propanoate–propan-1-ol.

In the aggregate, the prediction of the equilibrium data of these methyl propanoate–alkanol systems, both with the ASOG method and with the three cases chosen from the UNIFAC model, is good, with an overall mean error of less than 4% in every case. Neither method can therefore be viewed with more favor than the other, nor can any one case of the three presented by singled out in the case of the UNIFAC model since, with all certainty, the results of the predictions may differ greatly according to the family studied.

The azeotrope found for the system $x H_5C_2COOCH_3 + (1 - x)C_2H_5(OH)$ corresponds to a value of $x = y = 0.483$ and $T = 345.58$ K, a concentration that differs by, approximately, 7% from that presented by Horsley (*5*). The ASOG group contribution model predicts the azeotrope of the above-mentioned system under conditions of $T = 345.70$ K and $x = y = 0.422$, with an error of 12.6%, while, in the three UNIFAC model cases studied, the azeotrope value closest to the experimental one is achieved, under conditions of $T = 345.55$ K and $x = y = 0.505$, with an error of 4.6% in the estimation of the said singular point.

Registry No. EtOH, 64-17-5; PrOH, 71-23-8; methyl propanoate, 554-12-1.

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Gas Solubilities (H_2, He, N_2, CO, O_2, Ar, CO_2) in Organic Liquids at 293.2 K

Petra Lühring and Adrian Schumpe*

Technische Chemie, Universität Oldenburg, D-2900 Oldenburg, West Germany

Solubilities of hydrogen, helium, nitrogen, carbon monoxide, oxygen, and carbon dioxide in 25 pure organic liquids and in 2 binary mixtures have been determined at the temperature of 293.2 K. The results are compared to the available literature data, to the regular-solution theory, and to the scaled-particle theory.

Experimental gas solubilities in organic liquids are tabulated for many gas/liquid systems (*1*). However, in a recent study (*2*) on oxygen diffusivities in organic liquids, some of the data needed to evaluate the diffusivities from the measured transmissibilities were not available. The regular-solution theory and the scaled-particle theory were not always applicable, and in other cases their predictions differed considerably. Therefore, gas solubilities in organic liquids were studied experimentally in 89 different gas/liquid systems and compared to the two models.

Experimental Section

The gas solubilities were determined by a barometric method used already in a previous study (*3*). The measuring chamber was a glass vessel divided into chambers for the liquid ($V_L = 349.6$ cm^3) and the gas ($V_G = 598.9$ cm^3) by a horizontal glass plate with openings at the center and near the wall. The plate enabled the exact adjustment of the liquid level and inhibited premature gas absorption. The vessel was kept at a temperature of 293.2 ± 0.1 K by means of a jacket connected to a thermostat; furthermore, the apparatus was placed in a box with an internal air temperature of 293.2 ± 0.2 K. The substances were obtained from Merck at the highest available purity except for ligroin (alkanes with a bp range of 373–413 K).

A surplus volume of liquid was degassed by evacuation. The process was terminated once the correct liquid level was reached by evaporation of the liquid at its vapor pressure P_L. Dry gas of atmospheric pressure P_0 was slowly introduced into the head space. After pressure and temperature equilibration, the gas line was disconnected and a magnetic stirrer in the liquid was started. The liquid overflowed the plate and got

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* Address correspondence to this author at Gesellschaft für Biotechnologische Forschung (GBF), Mascheroder Weg 1, D-3300 Braunschweig, West Germany.

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