ISOBARIC VAPOR-LIQUID EQUILIBRIA FOR PROPYL METHANOATE+ (*n*-ALKANES, C_7 , C_8 , C_9) OR *n*-ALKANOLS (C_2 , C_3 , C_4)

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The compositions of the vapor-liquid equilibria have been obtained in a small capacity recirculating still for the binary mixtures composed of propyl methanoate with *n*-alkanes (heptane, octane, nonane) and *n*-alkanols (ethanol, propanol, butanol) at a constant pressure of 101.32 ± 0.02 kPa. Experimental data were thermodynamically verified and then correlated with suitable equations. The mixtures (x_1 propyl methanoate + x_2 *n*-heptane, or + x_2 ethanol, or + x_2 propan-1-ol) have an azeotrope at $x_1 = 0.786, 0.482$ and 0.852 , respectively. The predictions made by the ASOG and UNIFAC models can be considered acceptable.

Introduction

This work is part of a wide research project on vapor-liquid equilibrium (VLE) at constant pressure for binary mixtures of alkyl esters with other substances (*n*-alkanes, *n*-alkanols and chloroalkanes). In this sense, our working group has published much data on isobaric equilibrium of methyl, ethyl and propyl esters with alkanols¹²⁻¹⁴, and in order to complement this study, we are supplementing the experimental database with these substances. Our aim is to verify the accuracy of some theoretical models in the prediction of VLE. There are few VLE data for mixtures formed by alkyl methanoate with alkanes and alkanols in the literature. Therefore, in this work *T*-*x*-*y* data for propyl methanoate+*n*-alkanes (heptane, octane, nonane) or +*n*-alkanols (ethanol, propanol, butanol) at 101.32 kPa were determined experimentally.

With reference to these mixtures, some data are available for (propyl methanoate+*n*-propanol)⁵ at atmospheric pressure. The estimation for the formation of azeotrope in the mixture (propyl methanoate+*n*-heptane) made by Lecat, see Horsley⁸, shall be verified experimentally.

On the other hand, for chemical engineers, it is useful to know the prediction capability of certain theoretical models in order to make a quick investigation of many mixtures. The use of such models depends on a large VLE database. The experimental values will be compared with ASOG⁹, UNIFAC^{3, 7}) and Modified UNIFAC¹⁰) models.

1. Experimental Section

1.1 Chemicals

All products were of highest commercial purity, propyl methanoate (from Aldrich) and the *n*-alkanes and *n*-alkanols (from Fluka AG), and were degassed ultra-

sonically before use and stored in the dark for several days over molecular sieves (Union Carbide, type 0.3 nm, from Fluka AG). After these treatments, the physical characteristics of the pure substances used in this work are listed in **Table 1** together with literature values.

1.2 Apparatus and procedure

Vapor-liquid equilibrium measurements were carried out using a dynamic recirculating all-glass still described previously¹²). The still allows good mixing of both phases and their separation once they reach equilibrium. A calefactor resistance in the upper zone of the still prevents liquid drops and partial condensation in to the liquid phase. The boiling temperature *T* in the equilibrium still was measured with a digital Comark-6800 thermometer with an accuracy of ± 0.01 K, calibrated against a standard thermometer (ITS 90). The pressure *p* was maintained constant to within ± 0.02 kPa by an electronic regulator (Fisher).

The compositions of the liquid *x* and vapor *y* phases were determined by densimetry using an Anton-Paar DMA55 vibrating-tube densimeter calibrated with water and *n*-nonane and employing standard curves for density-concentration of each mixtures considered at the temperature 298.15 K. The uncertainty of composition measurements was estimated to be ± 0.001 mole-fraction.

2. Experimental Results and Treatment of Data

2.1 Vapor pressures

The vapor pressures p_i^0 of the pure liquids have an important effect on the computation of vapor-liquid equilibrium data. Therefore, in the same equilibrium still, new experimental data of the vapor pressures, p_i^0 of propyl methanoate were determined. **Table 2** lists the data obtained for propyl ester which were correlated through the Antoine equation:

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Table 1. Densities, ρ , refractive indices, n , and normal boiling point, T_b , of the chemicals used

	ρ (298.15 K) (kgm ⁻³)		n (D, 298.15 K)		T_b /K	
	exp.	lit.	exp.	lit.	exp.	lit.
Propyl methanoate ²¹⁾	899.22	899.6 ^{16, 21)}	1.3747	1.3750 ^{16, 21)}	353.79	353.97 ^{16, 21)}
<i>n</i> -Heptane	679.35	679.46 ¹⁶⁾ 679.51 ¹⁹⁾	1.3853	1.38511 ¹⁶⁾ 1.38519 ¹⁹⁾	371.54	371.57 ¹⁶⁾ 371.5519
<i>n</i> -Octane	698.44	698.62 ¹⁶⁾	1.3952	1.39505 ^{16, 1)}	398.91	398.82 ¹⁶⁾
<i>n</i> -Nonane	713.85	713.75 ¹⁶⁾ 713.81 ^{19, 1)}	1.4033	1.40311 ^{16, 1)} 1.40338 ¹⁹⁾	423.82	423.97 ¹⁶⁾ 423.95 ¹⁹⁾
Ethanol ²¹⁾	784.94	784.93 ¹⁶⁾ 785.09 ²¹⁾	1.3594	1.35941 ^{16, 21)} 1.3593 ¹⁹⁾	351.13	351.44 ^{16, 21)} 351.45 ¹⁹⁾
<i>n</i> -Propanol	799.54	799.60 ¹⁶⁾ 799.75 ²¹⁾	1.3833	1.38370 ^{16, 1)}	369.83	370.30 ¹⁶⁾ 370.35 ²¹⁾
<i>n</i> -Butanol	805.93	805.75 ¹⁶⁾ 806.0 ²¹⁾	1.3974	1.39741 ¹⁶⁾ 1.3971 ²¹⁾	390.81	390.87 ¹⁶⁾ 390.81 ²¹⁾

Table 2. Experimental vapor pressures, p_i^o , of propyl methanoate as a function of temperature, T . Antoine equation coefficients for the pure compounds, below.

T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa	T/K	p_i^o/kPa
337.38	58.94	345.93	79.55	353.75	102.73	360.57	127.07
338.58	61.54	346.79	81.91	354.34	104.67	361.04	128.95
339.24	63.01	347.78	84.62	354.70	105.84	361.68	131.50
340.12	65.01	348.65	87.08	355.51	108.60	362.23	133.78
340.73	66.45	349.48	89.56	356.24	111.13	362.72	135.78
341.49	68.20	350.49	92.50	357.05	113.97	363.11	137.42
342.40	70.28	351.08	94.28	357.60	115.96	363.51	139.06
342.90	71.60	351.64	96.02	358.29	118.48	364.02	141.22
343.46	73.01	351.87	96.75	358.84	120.52	364.43	143.00
344.30	75.26	352.57	98.94	359.47	122.90	364.85	144.82
345.34	77.87	353.55	102.03	360.04	125.06	365.28	146.71
A		B		C		$s(p_i^o)/kPa$	
Propyl methanoate		6.07003	1184.43	61.89	0.07	this work	
		5.97008	1132.30	68.35	1.02 ^a	(6)	
		6.16037	1226.68	58.39	0.95 ^a	(2)	
<i>n</i> -Heptane		6.01876	1264.37	56.51	-	(6)	
<i>n</i> -Octane		6.05632	1358.80	63.30	-	(6)	
<i>n</i> -Nonane		6.05932	1429.46	71.33	-	(6)	
Ethanol		7.1130	1513.02	55.15	-	(15)	
<i>n</i> -Propanol		6.8698	1434.94	74.98	-	(15)	
<i>n</i> -Butanol		6.9170	1572.51	70.04	-	(18)	

^a Differences with respect to experimental values above.

$$\log(p_i^o/kPa) = A - B/[(T/K) - C] \quad (1)$$

the constants A , B and C were calculated by a non-linear regression procedure¹¹⁾, whose values and the standard deviation, $s(p_i^o)$, are also shown in Table 2. The values of the Antoine constants used for the *n*-alkanes and *n*-alknols were obtained from the literature^{6, 15, 18)}.

2.2 Vapor-liquid equilibrium data

The experimental isobaric VLE data for the binary systems (x_1 propyl methanoate + x_2 *n*-alkanes or x_2 *n*-alknols)

Table 3. Experimental VLE data for the systems (x_1 Propyl methanoate + x_2 *n*-Alkane or *n*-Alkanol) at 101.32 kPa.

T/K	x_1	y_1	γ_1	γ_2
x_1 Propyl methanoate + x_2 <i>n</i> -Heptane				
371.54	0.0000	0.0000	-	1.000
368.66	0.0325	0.1004	1.957	1.013
364.10	0.0928	0.2444	1.901	1.033
362.08	0.1247	0.3068	1.886	1.056
359.96	0.1793	0.3836	1.750	1.063
358.17	0.2335	0.4480	1.653	1.088
356.50	0.3121	0.5151	1.497	1.124
354.87	0.4044	0.5774	1.362	1.194
354.25	0.4490	0.6040	1.308	1.235
353.88	0.4798	0.6212	1.274	1.267
353.72	0.4942	0.6282	1.257	1.286
353.52	0.5123	0.6381	1.239	1.307
353.38	0.5274	0.6468	1.226	1.322
352.94	0.5493	0.6581	1.202	1.348
352.86	0.5820	0.6750	1.175	1.397
352.48	0.5984	0.6830	1.159	1.422
352.30	0.6887	0.7307	1.097	1.589
352.27	0.7306	0.7525	1.066	1.690
352.19	0.7848	0.7854	1.038	1.841
352.21	0.8277	0.8153	1.021	1.979
352.35	0.8765	0.8566	1.008	2.136
352.53	0.9085	0.8847	0.998	2.306
352.77	0.9354	0.9127	0.993	2.455
353.10	0.9572	0.9377	0.986	2.617
353.45	0.9821	0.9717	0.985	2.813
353.79	1.0000	1.0000	1.000	-
x_1 Propyl methanoate + x_2 <i>n</i> -Octane				
398.91	0.0000	0.9717	0.985	2.813
393.45	0.0241	0.1421	1.936	1.023
388.50	0.0552	0.2735	1.904	1.033
384.40	0.0885	0.3827	1.775	1.030
378.55	0.1440	0.5075	1.686	1.050
374.15	0.1987	0.5941	1.611	1.065
371.09	0.2429	0.6432	1.554	1.097
368.99	0.2829	0.6807	1.498	1.113
366.53	0.3391	0.7205	1.420	1.150
365.20	0.3694	0.7396	1.391	1.175
364.40	0.3881	0.7506	1.376	1.193
363.26	0.4277	0.7702	1.325	1.224
362.28	0.4592	0.7842	1.294	1.259
361.39	0.4951	0.7981	1.255	1.303
360.77	0.5198	0.8088	1.234	1.326
360.29	0.5544	0.8191	1.189	1.376
359.48	0.5954	0.8331	1.154	1.440
358.60	0.6403	0.8487	1.123	1.517
357.89	0.6784	0.8605	1.098	1.605
356.90	0.7375	0.8793	1.065	1.765
356.23	0.7837	0.8961	1.043	1.891
355.70	0.8222	0.9097	1.026	2.040
354.86	0.8905	0.9374	1.002	2.372
354.44	0.9235	0.9533	0.966	2.575
354.04	0.9580	0.9722	0.991	2.836
353.61	0.9793	0.9863	0.993	2.877
353.79	1.0000	1.0000	1.000	-

nols) at (101.32 ± 0.02) kPa are given in Table 3. The activity coefficients γ_i in the liquid phase for each equilibrium stage were calculated as:

$$\ln \gamma_i = \ln \left(\frac{p y_i}{p_i^o x_i} \right) + \frac{(B_{ii} v_i^L)(p - p_i^o)}{RT} + \frac{p}{2RT} \sum_j \sum_k y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (2)$$

where:

$$\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj} \quad (3)$$

The molar volumes v_i^L of the saturated liquid were estimated by the modified Rackett equation¹⁷⁾. The second virial coefficients B_{ij} for both the pure components and the

x_1 Propyl methanoate + x_2 n-Nonane				
423.82	0.0000	0.0000	-	1.000
405.85	0.0657	0.4284	1.591	1.016
402.25	0.0807	0.4938	1.618	1.020
399.32	0.0951	0.5428	1.616	1.024
397.75	0.1031	0.5641	1.607	1.034
395.90	0.1142	0.5898	1.586	1.044
391.55	0.1411	0.6456	1.561	1.070
382.15	0.2127	0.7500	1.528	1.130
375.55	0.2772	0.8142	1.519	1.157
372.10	0.3298	0.8464	1.461	1.171
370.30	0.3618	0.8601	1.424	1.197
368.55	0.3960	0.8727	1.388	1.230
366.95	0.4325	0.8850	1.349	1.258
365.50	0.4694	0.8950	1.312	1.299
364.05	0.5124	0.9070	1.271	1.325
362.85	0.5518	0.9146	1.234	1.387
361.80	0.5886	0.9217	1.203	1.446
360.85	0.6287	0.9285	1.167	1.520
359.90	0.6643	0.9345	1.145	1.598
359.25	0.7009	0.9408	1.114	1.667
358.55	0.7324	0.9457	1.095	1.757
357.85	0.7715	0.9520	1.070	1.871
356.90	0.8169	0.9596	1.048	2.048
356.13	0.8565	0.9678	1.033	2.147
355.49	0.8907	0.9738	1.020	2.359
354.85	0.9323	0.9817	1.002	2.735
353.79	1.0000	1.0000	1.000	-
x_1 Propyl methanoate + x_2 -Ethanol				
351.13	0.0000	0.0000	-	1.000
349.67	0.0314	0.0779	2.777	1.005
349.37	0.0439	0.0973	2.506	1.008
349.08	0.0536	0.1142	2.432	1.011
348.50	0.0739	0.1515	2.386	1.013
347.95	0.0962	0.1871	2.306	1.016
347.68	0.1115	0.2083	2.235	1.017
347.10	0.1451	0.2480	2.086	1.028
346.78	0.1631	0.2667	2.017	1.037
346.45	0.1869	0.2919	1.949	1.044
346.23	0.2109	0.3138	1.817	1.052
345.97	0.2366	0.3338	1.790	1.067
345.65	0.2835	0.3683	1.666	1.092
345.49	0.3079	0.3848	1.612	1.108
345.31	0.3582	0.4161	1.508	1.142
345.17	0.4168	0.4467	1.398	1.197
345.13	0.4536	0.4669	1.345	1.233
345.15	0.4984	0.4904	1.285	1.283
345.24	0.5396	0.5121	1.236	1.333
345.36	0.5815	0.5353	1.194	1.390
345.63	0.6325	0.5639	1.146	1.469
345.90	0.6728	0.5887	1.115	1.539
346.75	0.7574	0.6484	1.060	1.713
348.10	0.8347	0.7250	1.029	1.862
348.70	0.8608	0.7542	1.017	1.929
350.68	0.9215	0.8488	1.002	1.945
350.87	0.9268	0.8576	1.001	1.950
351.47	0.9433	0.8860	0.996	1.968
351.65	0.9467	0.8921	0.994	1.968
353.79	1.0000	1.0000	1.000	-

x_1 Propyl methanoate + x_2 n-Propanol				
369.83	0.0000	0.0000	-	1.000
367.88	0.0276	0.0840	1.942	1.017
365.88	0.0671	0.1852	1.869	1.018
365.55	0.0748	0.1998	1.826	1.021
362.38	0.1619	0.3454	1.605	1.043
361.25	0.1912	0.3902	1.589	1.053
359.95	0.2427	0.4543	1.517	1.060
359.48	0.2635	0.4743	1.480	1.069
358.88	0.2904	0.4987	1.439	1.084
357.67	0.3575	0.5517	1.343	1.124
357.28	0.3794	0.5687	1.320	1.138
356.78	0.4121	0.5902	1.281	1.165
356.35	0.4437	0.6100	1.247	1.192
355.96	0.4740	0.6289	1.218	1.219
355.48	0.5156	0.6526	1.180	1.263
355.11	0.5536	0.6730	1.147	1.310
354.68	0.5947	0.6981	1.123	1.356
354.33	0.6354	0.7221	1.099	1.407
354.05	0.6804	0.7443	1.068	1.494
353.76	0.7219	0.7700	1.051	1.563
353.55	0.7678	0.7950	1.027	1.682
353.36	0.8181	0.8269	1.009	1.827
353.27	0.8698	0.8653	0.996	1.993
353.30	0.9265	0.9126	0.985	2.286
353.79	1.0000	1.0000	1.000	-
x_1 Propyl methanoate + x_2 n-Butanol				
390.81	0.0000	0.0000	-	1.000
383.97	0.0659	0.2412	1.511	1.011
382.06	0.0911	0.3124	1.488	1.010
378.99	0.1306	0.4021	1.450	1.030
373.20	0.2360	0.5643	1.319	1.070
370.35	0.3032	0.6357	1.254	1.100
369.21	0.3313	0.6617	1.234	1.115
368.11	0.3621	0.6865	1.209	1.133
367.10	0.3873	0.7059	1.197	1.154
365.97	0.4176	0.7284	1.184	1.175
363.77	0.4906	0.7726	1.140	1.235
362.75	0.5293	0.7931	1.119	1.271
361.85	0.5644	0.8104	1.101	1.308
360.85	0.6090	0.8306	1.078	1.360
359.97	0.6465	0.8443	1.060	1.438
359.18	0.6842	0.8587	1.044	1.512
358.31	0.7210	0.8719	1.033	1.613
357.76	0.7524	0.8843	1.021	1.683
357.21	0.7809	0.8939	1.012	1.788
356.73	0.8078	0.9036	1.004	1.893
356.19	0.8382	0.9127	0.994	2.087
355.50	0.8702	0.9257	0.992	2.285
354.99	0.9000	0.9389	0.989	2.492
353.79	1.0000	1.0000	1.000	-

mixtures were calculated according to Tsonopoulos' empirical correlations²⁰). The vapor pressures of the pure components p_i^o were obtained by use of the Antoine equation with the constants from Table 2. All mixtures present positive deviations from ideality, except at high ester concentrations where some association effects appear. The thermodynamic consistency of the data was tested by using the point-to-point procedure as described by Fredenslund *et al.*⁴) Binary mixtures studied here proved to be consistent with that method, presenting deviations in each vapor-phase point near to the limits established for the test.

The reduction of the equilibrium data was carried out for the dimensionless function g^E/RT versus liquid-phase mole fraction with the Margules, van Laar, Wilson,

NRTL, UNIQUAC and Redlich-Kister equations, and others used by us in previously¹²⁻¹⁵). The form is:

$$Q = z(1-z) \sum A_i \{z/[z+k(1-z)]\}^i \quad (4)$$

where Q represents the fitting function and z is the variable. The parameters obtained for each equations mentioned above and Eq. (4) are shown in **Table 4** along with the standard deviations between the values of g^E/RT obtained from γ_i , Eq. (2), and those calculated. The results indicate that all equations, except that of van Laar, are equally suitable to represent the data, although it can be observed that the best correlation corresponds to Eq. (4). Thus, this relationship was employed to fit the composition data obtained directly through (y_1-x_1) vs x_1 .

The plot of the function obtained for each system appears in **Fig. 1**. The correlations for y_1 versus x_1 and T versus x_1 were used to determine precise location of the azeotropes, such as in previous work¹⁴). The values found are shown in **Table 5**. The difference between our azeotropes experimental values and those of Lecat, see Horsley⁸), for $(x_1$ propyl methanoate + x_2 n-heptane) were

Table 4. Correlation parameters and standard deviations, s

x_1 Propyl Methanoate + $x_2 n$ -Heptane							s (g ^E /RT)
Margules	$A_{12} = 1.004$	$A_{21} = 0.887$					0.0059
van Laar	$A_{12} = 2.374$	$A_{21} = 0.216$					0.1109
Wilson	$A_{12} = 0.492$	$A_{21} = 0.674$					0.0057
NRTL ($\alpha = 0.47$)	$\tau_{12} = 0.398$	$\tau_{21} = 0.693$					0.0058
UNIQUAC ($z = 10$)	$\tau_{12} = 1.273$	$\tau_{21} = 0.542$					0.0059
Redlich-Kister	$A_0 = 0.933$	$A_1 = 0.049$	$A_2 = 0.101$	$A_3 = -0.352$			0.0035
Equation (4)	$A_0 = 1.431$	$A_1 = -0.496$			$k = 0.057$		0.0044
x_1 Propyl Methanoate + $x_2 n$ -Octane							s (g ^E /RT)
Margules	$A_{12} = 0.893$	$A_{21} = 0.993$					0.0045
van Laar	$A_{12} = 1.469$	$A_{21} = 0.848$					0.0384
Wilson	$A_{12} = 0.654$	$A_{21} = 0.512$					0.0046
NRTL ($\alpha = 0.47$)	$\tau_{12} = 0.663$	$\tau_{21} = 0.422$					0.0046
UNIQUAC ($z = 10$)	$\tau_{12} = 1.178$	$\tau_{21} = 0.610$					0.0045
Redlich-Kister	$A_0 = 0.943$	$A_1 = 0.050$					0.0045
Equation (4)	$A_0 = 4.036$	$A_1 = -7.124$	$A_2 = 4.088$		$k = 0.028$		0.0028
x_1 Propyl Methanoate + $x_2 n$ -Nonane							s (g ^E /RT)
Margules	$A_{12} = 0.967$	$A_{21} = 1.163$					0.0087
van Laar	$A_{12} = 0.790$	$A_{21} = 1.229$					0.0222
Wilson	$A_{12} = 0.655$	$A_{21} = 0.423$					0.0092
NRTL ($\alpha = 0.47$)	$\tau_{12} = 0.843$	$\tau_{21} = 0.425$					0.0091
UNIQUAC ($z = 10$)	$\tau_{12} = 1.184$	$\tau_{21} = 0.582$					0.0088
Redlich-Kister	$A_0 = 1.076$	$A_1 = -0.017$	$A_2 = -0.054$	$A_3 = 0.310$			0.0069
Equation (4)	$A_0 = -0.444$	$A_1 = 7.019$	$A_2 = -10.593$	$A_3 = 5.21$	$k = 0.249$		0.0037
x_1 Propyl Methanoate + x_2 Ethanol							s (g ^E /RT)
Margules	$A_{12} = 1.102$	$A_{21} = 0.874$					0.0053
van Laar	$A_{12} = 1.044$	$A_{21} = 1.029$					0.0077
Wilson	$A_{12} = 0.428$	$A_{21} = 0.714$					0.0059
NRTL ($\alpha = 0.47$)	$\tau_{12} = 0.336$	$\tau_{21} = 0.836$					0.0058
UNIQUAC ($z = 10$)	$\tau_{12} = 0.336$	$\tau_{21} = 0.836$					0.0056
Redlich-Kister	$A_0 = 1.003$	$A_1 = -0.024$	$A_2 = -0.083$	$A_3 = -0.250$			0.0027
Equation (4)	$A_0 = 1.103$	$A_1 = -0.881$	$A_2 = 2.327$	$A_3 = -2.258$	$k = 3.036$		0.0015
x_1 Propyl Methanoate + $x_2 n$ -Propanol							s (g ^E /RT)
Margules	$A_{12} = 1.102$	$A_{21} = 0.873$	0.0054				
van Laar	$A_{12} = 1.216$	$A_{21} = 0.661$	0.0220				
Wilson	$A_{12} = 0.594$	$A_{21} = 0.668$	0.0044				
NRTL ($\alpha = 0.47$)	$\tau_{12} = 0.372$	$\tau_{21} = 0.516$	0.0044				
UNIQUAC ($z = 10$)	$\tau_{12} = 0.733$	$\tau_{21} = 0.995$	0.0045				
Redlich-Kister	$A_0 = 0.791$	$A_1 = 0.054$	$A_2 = 0.032$	$A_3 = -0.251$			0.0025
Equation (4)	$A_0 = 1.164$	$A_1 = -2.003$	$A_2 = 3.428$	$A_3 = -1.874$	$k = 0.531$		0.0021
x_1 Propyl Methanoate + $x_2 n$ -Butanol							s (g ^E /RT)
Margules	$A_{12} = 0.539$	$A_{21} = 0.854$					0.0047
van Laar	$A_{12} = 0.575$	$A_{21} = 0.925$					0.0054
Wilson	$A_{12} = 1.050$	$A_{21} = 0.381$					0.0035
NRTL ($\alpha = 0.47$)	$\tau_{12} = 0.932$	$\tau_{21} = -0.039$					0.0038
UNIQUAC ($z = 10$)	$\tau_{12} = 0.541$	$\tau_{21} = 1.322$					0.0038
Redlich-Kister	$A_0 = 0.681$	$A_1 = 0.147$	$A_2 = 0.117$				0.0029
Equation (4)	$A_0 = 0.611$	$A_1 = 0.504$			$k = 6.046$		0.0024

smaller than 7 % however, this represents about 1.0 K. For the mixture (x_1 propyl methanoate + $x_2 n$ -propanol), the bibliography⁵⁾ shows only four points which have been represented in Fig. 1 (b); the azeotropic point estimated by the correlation used from the literature was 0.985 which is different from our experimental value.

3. Prediction of VLE with Different Group Contribution Models

In Table 6 an evaluation of the experimental versus predicted azeotropes is shown. The widely used group-contribution models in were applied, such as ASOG⁹⁾, UNIFAC^{3, 7)}, and Modified UNIFAC¹⁰⁾. In all cases, the predictions were evaluated by comparison with the activity coefficients, γ_i , and the concentration values of the vapor phase, y_i , obtained implicitly by applying Eqs. (2) and (3). Table 6 gives average percentage errors in estimation of the

activity coefficients for all systems. The average errors for the y_i -values showed a similar trend to the corresponding γ_i -values. As a general comment, the predictions obtained with the different models appear to be acceptable. Table 5 shows the predictions of the azeotrope points for each mixture. The major error appears in the mixture (propyl methanoate + n -propanol) with a difference close to 0.1 mole fraction. However, the estimation of the azeotropic temperature is excellent in all cases.

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Nomenclature

A, B, C	= Antoine constants	[-]
A_i	= coefficients in Eq. (4)	[-]
B_{ij}	= cross-virial coefficient	[m ³ kmol ⁻¹]
e	= average percent error	[-]
k	= parameter in Eq. (4)	[-]

Fig. 1 Plot of $(y_1 - x_1)$ vs x_1 for the mixtures studied employing Eq. (4). (a), $(x_1 \text{ propyl methanoate} + x_2 n\text{-alkanes})$; (b), $(x_1 \text{ propyl methanoate} + x_2 n\text{-alkanols})$; (●), experimental points from ref. 5.

p	= total pressure	[kPa]
p_i^o	= vapor pressure of pure component i	[kPa]
R	= universal gas constant	[JK ⁻¹ kmol ⁻¹]
s	= standard deviation	[-]
T	= temperature	[K]
T_b	= boiling temperature of pure component i	[K]
V_i^L	= molar volume of pure component i	[m ³ kmol ⁻¹]
x	= liquid-phase mole fraction	[-]
y	= vapor-phase mole fraction	[-]
ρ	= density	[kg m ⁻³]
γ_i	= activity coefficient of component i	[-]

Table 5. Azeotropes obtained for the binary mixtures studied at 101.32 kPa

Mixture	exptl.	$x_1 = y_1$ (at T/K) lit.	predicted
x_1 Propyl Methanoate + $x_2 n$ -Heptane	0.786 (352.20 K)	0.736 ⁸⁾	0.829 (352.3 K) ASOG ⁹⁾ 0.839 (352.2 K) UNIFAC ^{3, 7)} 0.761 (352.2 K) M. UNIFAC ¹⁰⁾
+ x_2 Ethanol	0.482 (345.12 K)		0.408 (345.2 K) ASOG ⁹⁾ 0.483 (345.1 K) UNIFAC ^{3, 7)} 0.474 (345.1 K) M. UNIFAC ¹⁰⁾
+ $x_2 n$ -Propanol	0.852 (353.20 K)	0.985 ⁵⁾	0.958 (353.5 K) ASOG ⁹⁾ 0.957 (353.7 K) UNIFAC ^{3, 7)} 0.958 (353.4 K) M. UNIFAC ¹⁰⁾

Table 6. Average per cent errors, $\bar{e}$, obtained in prediction of γ_i for the isobaric VLE at 101.32 kPa using different theoretical models.

Mixture	ASOG ⁹⁾	UNIFAC ^{3, 7)}	Modified UNIFAC ¹⁰⁾
Propyl Methanoate +			
n -Heptane	4.3 (γ_1)	5.4 (γ_2)	7.4 (γ_1)
n -Octane	8.6 (γ_1)	6.2 (γ_2)	11.2 (γ_1)
n -Nonane	11.7 (γ_1)	7.5 (γ_2)	12.9 (γ_1)
Ethanol	8.0 (γ_1)	3.0 (γ_2)	3.0 (γ_1)
n -Propanol	1.7 (γ_1)	5.4 (γ_2)	7.8 (γ_1)
n -Butanol	4.0 (γ_1)	10.6 (γ_2)	10.0 (γ_1)

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