R	gas constant, cm^3 torr/(mol K)
T	temperature, K
V	liquid molar volume, cm^3/mol
x, y	liquid and vapor molar fractions, respectively

Greek Letters

γ	activity coefficients
ρ	density $1/V$, mol/cm^3

Subscripts

1, 2	components 1 and 2, respectively
i, j	components i and j, respectively
exptl, calcd	experimental or calculated quantity, respectively

Superscripts

L	liquid-phase property
V	vapor-phase property
∞	at infinite diluted conditions

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Isothermal Vapor–Liquid Equilibria in Binary Systems Formed by Esters with Alkenes

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Since no vapor–liquid equilibrium (VLE) data are available for ester–alkene systems, isothermal vapor–liquid equilibrium data have been measured for the binary systems methyl acetate–1-hexene (50 °C), 1-hexene–ethyl acetate (60 °C), ethyl acetate–1-octene (75 °C), and butyl acetate–1-decene (90 °C). Thermodynamic consistency was checked by two methods and the data were correlated by using different expressions for the excess Gibbs energy. The data were used for the determination of the C=C–CCOO interaction parameters of the UNIFAC method, which are important, e.g., for the prediction of the VLE behavior of vinyl acetate systems.

Introduction

Design of distillation columns requires the knowledge of vapor–liquid equilibria. With the recent expressions for the excess Gibbs energy (e.g., Wilson (*18*), NRTL (*19*), UNIQUAC (*20*)) multicomponent systems can be described by using binary data alone. Although a lot of binary data have been published (*1–3*), there is often a lack of data. In these cases the real behavior of the missing binary data must be estimated by using prediction methods, such as the group contribution methods ASOG (*4*, *5*) or UNIFAC (*6–9*). In these methods, the mixture is assumed to consist not of molecules but of the functional groups which, when added, form the parent molecules. This has the advantage that a large number of mixtures of interest in chemical technology can be described in terms of relatively few parameters characterizing the interaction between the groups.

These parameters have to be determined from experimental information. In the case of the UNIFAC method, the whole information of the Dortmund Data Bank (*10*, *11*) has been used. In spite of the large data base there are a lot of gaps in the parameter table for group combinations where no data (or no reliable data) are available in the literature.

Table I. Pure Components

component	supplier	type of column	grade of purification, %
1-hexene	EGA Chemie	*a*	>99.99
1-octene	Merck AG	*a*	>99.99
1-decene	Merck AG	*a*	>99.99
methyl acetate	DEGUSSA	*b*	>99.99
ethyl acetate	Merck AG	*b*	>99.99
butyl acetate	Riedel de Haen	*b*	>99.99

[a] Wire band column (length, 1000 mm; number of theoretical plates, approximately 55). [b] Packed column (diameter, 30 mm; length, 1000 mm; SS 316-helix packing).

The purpose of this investigation was to enable determination of the interaction parameters between the C=C and the CCOO group and thus fill one of the gaps in the UNIFAC parameter table. Therefore, the above-mentioned binary systems have been measured.

Experimental Section

Purification of the Components. All chemicals were obtained from commercial sources and were further purified by rectification in a packed or a wire band column, and the purity was tested by gas chromatography. Table I shows the supplier of the different chemicals and the grade of purification.

Analysis. Liquid and vapor compositions were determined with a digital densimeter (DMA02D by Heraeus/Paar). It was calibrated by using air and doubly distilled water. The density measurement was carried out at 20 ± 0.01 °C. The precision at this temperature was better than 10^{-4} g/cm^3. The calibration curves were attained by measuring weighed samples of the

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Table II. Experimental Data and Fitted Parameters for the System Methyl Acetate (1)-1-Hexene (2) at 50 °C

	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.8399	1.0720		0.0047
Van Laar	0.8468	1.0838		0.0047
Wilson	473.8652	259.2210		0.0047
NRTL	619.9473	80.0781	0.2980	0.0047
UNIQUAC	43.0213	180.6381		0.0047
UNIFAC				0.0201

P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
485.18	0.0	0.0	696.75	0.5417	0.5775
493.09	0.0085	0.0239	698.63	0.6159	0.6172
505.35	0.0250	0.0648	696.00	0.6967	0.6640
539.33	0.0686	0.1599	690.45	0.7611	0.7039
568.95	0.1087	0.2278	680.18	0.8163	0.7455
586.50	0.1369	0.2679	671.70	0.8557	0.7814
609.56	0.1820	0.3228	660.86	0.8904	0.8167
630.00	0.2285	0.3695	652.12	0.9143	0.8477
654.56	0.2948	0.4259	641.55	0.9344	0.8751
666.45	0.3407	0.4592	630.83	0.9506	0.9008
683.74	0.4147	0.5064	617.93	0.9696	0.9354
689.33	0.4627	0.5345	595.05	1.0000	1.0000

Table III. Experimental Data and Fitted Parameters for the System 1-Hexene (1)-Ethyl Acetate (2) at 60 °C

	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.6600	0.6817		0.0044
Van Laar	0.6595	0.6822		0.0044
Wilson	55.0482	432.7491		0.0044
NRTL	272.9532	196.3981	0.3006	0.0044
UNIQUAC	200.2223	−52.7351		0.0044
UNIFAC				0.0086

P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
420.60	0.0	0.0	639.00	0.4271	0.5655
436.84	0.0181	0.0536	651.90	0.4852	0.6042
451.50	0.0332	0.0935	666.64	0.5632	0.6542
468.26	0.0545	0.1431	676.95	0.6198	0.6896
481.50	0.0725	0.1813	684.49	0.6802	0.7283
504.75	0.1062	0.2424	689.70	0.7367	0.7663
524.59	0.1378	0.2915	694.05	0.7995	0.8111
546.75	0.1768	0.3438	694.95	0.8499	0.8504
568.13	0.2211	0.3945	693.34	0.8923	0.8867
592.65	0.2778	0.4463	690.90	0.9330	0.9254
608.18	0.3201	0.4861	687.53	0.9757	0.9713
624.00	0.3722	0.5267	685.50	1.0000	1.0000

binary alkene–ester mixture. The measurements of the density (composition) of the equilibrium samples were repeated more than twice.

Vapor–Liquid Equilibrium Measurements. Vapor–liquid equilibrium measurements were performed for four binary systems at isothermal conditions, where as pressure measurement device a precision mercury manometer (Wallace and Tiernan) was used as described in ref *12*.

Equilibrium was attained in an all-glass equilibrium still with circulation of both the vapor and liquid phases. The apparatus has been described earlier (*12*). For each data point approximately 45 min elapsed before equilibrium was attained and samples were taken by syringes.

The obtained data were checked for thermodynamic consistency by using the integral test (*13*) and the point-to-point test developed by Van Ness et al. (*14*) and modified by Christiansen and Fredenslund (*15*).

All data sets passed the consistency tests with good results using the criteria given in (*3*).

Results

The experimental data and the fitted parameters for the Margules (*16*), Van Laar (*17*), Wilson (*18*), NRTL (*19*) and UNIQUAC (*20*) equations are given in Tables II–V together with the mean deviation of the vapor-phase mole fraction.

Table IV. Experimental Data and Fitted Parameters for the System Ethyl Acetate (1)-1-Octene (2) at 75 °C

	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.4532	0.5879		0.0031
Van Laar	0.4606	0.5865		0.0030
Wilson	349.6978	60.2397		0.0030
NRTL	487.0795	−77.2810	0.2974	0.0030
UNIQUAC	−58.3286	178.3416		0.0030
UNIFAC				0.0087

P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
169.50	0.0	0.0	443.20	0.3480	0.7234
172.00	0.0031	0.0186	483.30	0.4254	0.7669
183.80	0.0154	0.0886	507.30	0.4705	0.7907
194.60	0.0269	0.1473	530.40	0.5147	0.8125
212.10	0.0447	0.2291	590.00	0.6632	0.8770
231.00	0.0640	0.3015	610.00	0.7141	0.8951
256.90	0.0918	0.3869	628.20	0.7647	0.9140
282.60	0.1201	0.4574	648.70	0.8150	0.9320
315.50	0.1595	0.5336	663.40	0.8602	0.9477
348.70	0.2031	0.5941	673.25	0.8909	0.9585
376.60	0.2409	0.6379	685.05	0.9238	0.9710
399.50	0.2780	0.6710	711.00	1.0000	1.0000
421.20	0.3083	0.6966			

Table V. Experimental Data and Fitted Parameters for the System Butyl Acetate (1)-1-Decane (2) at 90 °C

	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.3732	0.4126		0.0039
Van Laar	0.3757	0.4112		0.0039
Wilson	346.0209	−43.9474		0.0039
NRTL	259.7746	38.0567	0.3004	0.0039
UNIQUAC	−113.4702	194.6985		0.0039
UNIFAC				0.0067

P, mmHg	x_1	y_1	P, mmHg	x_1	y_1
55.24	0.0	0.0	175.00	0.5725	0.8400
59.85	0.0174	0.0952	174.80	0.5780	0.8417
65.60	0.0392	0.1920	182.80	0.6299	0.8640
75.86	0.0805	0.3335	186.70	0.6796	0.8854
86.75	0.1234	0.4394	192.84	0.6982	0.8906
89.80	0.1365	0.4630	202.00	0.7454	0.9138
99.95	0.1727	0.5316	203.00	0.7535	0.9117
109.09	0.2193	0.5942	205.77	0.7848	0.9239
120.90	0.2730	0.6542	212.13	0.8204	0.9362
126.35	0.3103	0.6797	212.38	0.8288	0.9390
129.05	0.3161	0.6985	216.75	0.8607	0.9500
135.75	0.3458	0.7178	220.00	0.8804	0.9575
140.76	0.3808	0.7364	221.25	0.8917	0.9618
141.55	0.3810	0.7402	225.20	0.9223	0.9730
148.70	0.4205	0.7637	227.40	0.9320	0.9771
158.05	0.4688	0.7948	233.35	0.9650	0.9888
157.90	0.4715	0.7922	236.20	1.0000	1.0000
166.90	0.5258	0.8188			

Table VI. Pure-Component Properties

component i	v_i	r_i	q_i
1-hexene	125.90	4.2697	3.644
1-octene	157.86	5.6185	4.724
1-decene	190.35	6.9673	5.804
methyl acetate	79.84	2.8042	2.576
ethyl acetate	98.49	3.4786	3.116
butyl acetate	132.55	4.8274	4.196

For fitting the parameters, we used the obtained pure-component vapor pressure and the following objective function F:

$$F = \sum_{i}^{\mathrm{NDP}} \sum_{j}^{\mathrm{NC}} [(\gamma_{i,\mathrm{exptl}} - \gamma_{i,\mathrm{calcd}})/\gamma_{i,\mathrm{exptl}}]^2$$

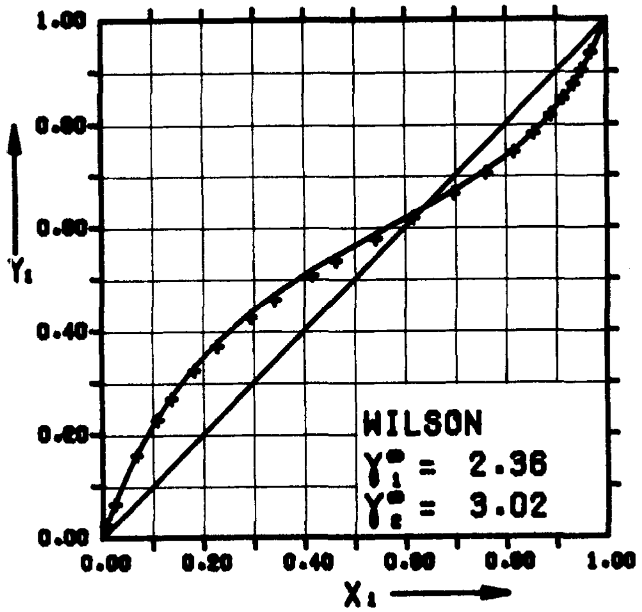

Figure 1. *y–x* diagram for the system methyl acetate (1)–1-hexene (2) at 50 °C.

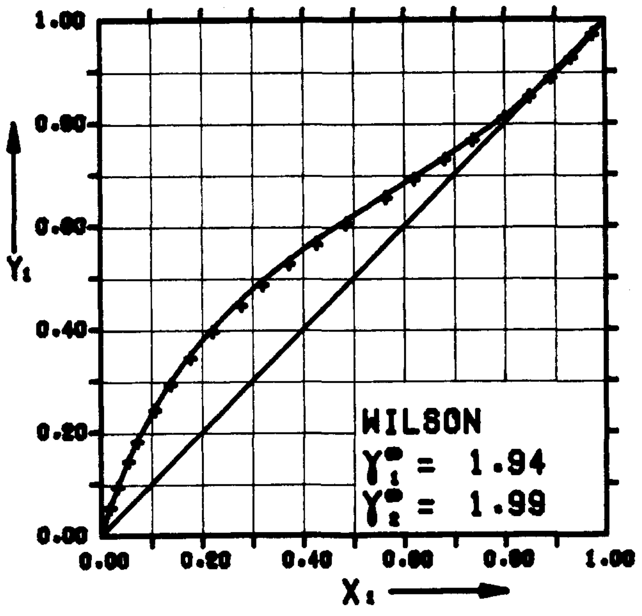

Figure 2. *y–x* diagram for the system 1-hexene (1)–ethyl acetate (2) at 60 °C.

where NDP = number of data points, NC = number of components, and vapor-phase ideality was assumed. For the equation based on the local composition concept (*2*, *3*) A_{ij} in Tables II–V has the following meaning: Wilson, $A_{ij} = (\lambda_{ij} - \lambda_{ii})$ cal/mol; NRTL, $A_{ij} = (g_{ij} - g_{jj})$ cal/mol; UNIQUAC, $A_{ij} = (u_{ij} - u_{jj})$ cal/mol. The required pure-component properties for the Wilson and UNIQUAC equations are given in Table VI.

Figures 1–4 show the *y–x* diagrams of the different systems, where the experimental data are given by the plus sign and the calculated results are represented by the continuous line. The calculated values were always generated by using the model which gave the lowest mean deviation between the experimental and calculated vapor-phase mole fractions.

Furthermore, in all diagrams the calculated activity coefficients at infinite dilution are given for the chosen model. In the systems methyl acetate–1-hexene and 1-hexene–ethyl acetate azeotropic behavior was found.

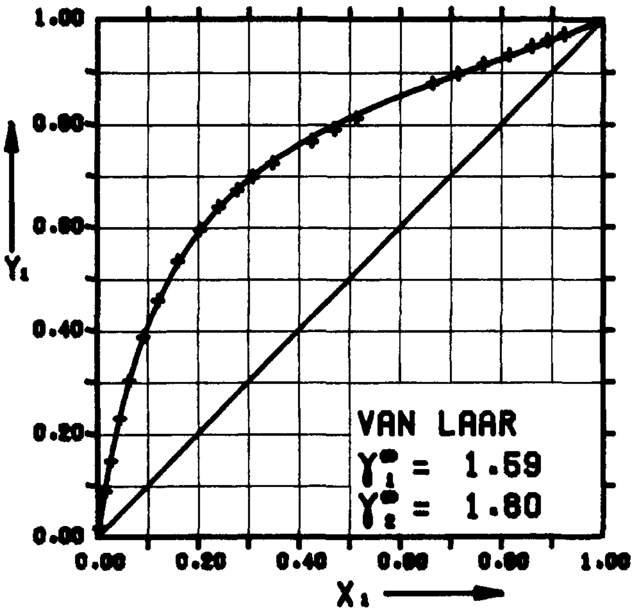

Figure 3. *y–x* diagram for the system ethyl acetate (1)–1-octene (2) at 75 °C.

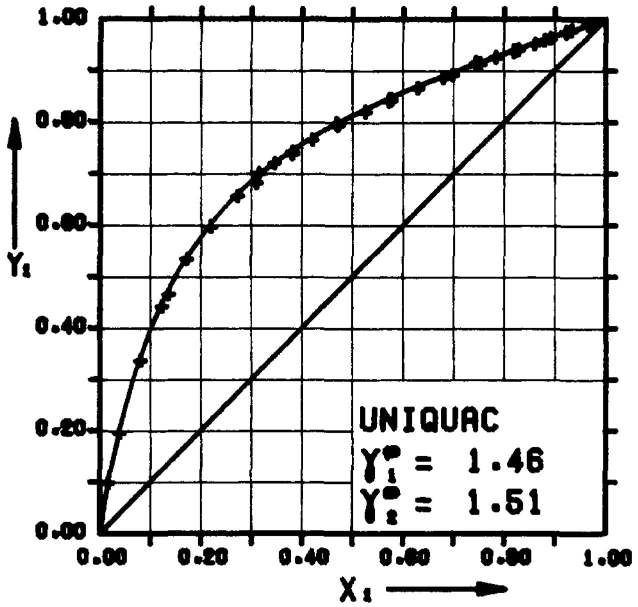

Figure 4. *y–x* diagram for the system butyl acetate (1)–1-decene (2) at 90 °C.

All these data were used to determine the missing group interaction parameters between the C=C and the ester group for the UNIFAC method (*9*). The new UNIFAC parameters are

$$a_{\mathrm{C{=}C,CCOO}} = 71.23\ \mathrm{K} \qquad a_{\mathrm{CCOO,C{=}C}} = 269.3\ \mathrm{K}$$

All other group interaction parameters were taken from ref *9*. The mean deviations in the vapor-phase mole fraction using these parameters are given in Tables II–V for the different binary systems.

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Glossary

A_{ij}	parameters used in the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations
F	objective function

g_{ij}	interaction parameter in the NRTL equation
u_{ij}	interaction parameter in the UNIQUAC equation
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
v_i	liquid molar volume of component i
r_i	relative van der Waals volume of component i
q_i	relative van der Waals surface area of component i

Greek Letters

α_{12}	nonrandomness parameter in NRTL equation
γ_i	activity coefficient of component i
λ_{ij}	interaction parameter in the Wilson equation

Subscripts

exptl	experimental
calcd	calculated

Superscript

∞	value at infinite dilution

Registry No. 1-Hexene, 592-41-6; 1-octene, 111-66-0; 1-decene, 872-05-9; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; butyl acetate, 123-86-4.

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Gibbs Excess Free Energy of Methylcyclohexane + Benzene and Methylcyclohexane + Toluene Mixtures at 348.15 K

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Vapor pressures as a function of composition and at 348.15 K were measured for the binary mixtures consisting of methylcyclohexane + benzene (MC + B) and methylcyclohexane + toluene (MC + T). Values for the Gibbs excess free energy for these mixtures were calculated and the results compared to those predicted by applying Flory's theory to the same mixtures and other binary mixtures made up of either *n*-heptane or methylcyclohexane + *o*-, + *m*-, and + *p*-xylenes.

This paper deals with alicyclic + aromatic hydrocarbon binary mixtures. In particular we have selected methylcyclohexane + benzene (MC + B) and + toluene (MC + T) as representative mixtures.

Liquid-vapor equilibrium data allow calculation of Gibbs excess free energy, G^E, a characteristic thermodynamic quantity suitable to study thermodynamic properties of liquid solutions.

Thus, we have measured at 348.15 K total vapor pressures, p, for the two aforementioned systems as a function of liquid and vapor composition, x and y, respectively, and throughout the whole concentration range.

The data herein contained and others previously published (*1*, *2*) for *n*-heptane and methylcyclohexane with *o*-, *m*-, and *p*-xylenes can be used to check liquid solution theories. From them, we have selected Flory's theory (*3*, *4*) as the most sensitive to G^E value changes.

Experimental Results

Vapor pressure was measured by a dynamic method. The ebulliometer was similar to one described in a previous paper (*5*).

The sources of the chemicals were the following: methylcyclohexane from Hopkin and Williams (for chromatography), benzene from Carlo Erba (for chromatography), and toluene from Merck (Uvasol). They were further purified by fractional distillation in a 35-theoretical-plate column at a 120 reflux ratio. Only the middle fraction was used, after it was dried over sodium wire. Purity of the used products, estimated by GLC using a flame ionization detector, was better than 99.8 mol %. The density at 298.15 K, the refractive index at 303.15 K, and the vapor pressure at various temperatures were reported earlier (*2*, *6*, *7*) where the data were compared to similar ones available in the published literature. Individual vapor pressure measurements are accurate to ±7 Pa, mole fractions to $\pm 5 \times 10^{-4}$, and temperature to ±0.01 K. It is estimated that G^E is accurate to better than 2.1 J mol^{-1} for the MC + B system and to better than 0.9 J mol^{-1} for the T + MC system.

Vapor- and liquid-phase composition at equilibrium was determined by refractive index measurements, n_D, at 303.15 K. This meant that we had to obtain first a calibrated curve of n_D

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