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Extension of UNIFAC by Headspace Gas Chromatography

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Isothermal vapor–liquid equilibrium data for the following binary systems have been obtained by means of headspace gas chromatography: ethanol–toluene (45.4 °C), 1-propanol–*n*-decane (93.0 °C), valeraldehyde–1-octene (81.8 °C), 1-hexene–valeraldehyde (40.3 °C), butyraldehyde–1-octene (55.4 °C), valeraldehyde–1-decene (80.3 °C), ethyl acetate–valeraldehyde (49.3 °C), valeraldehyde–butyl acetate (80.4 °C), and butyraldehyde–butyl acetate (52.8 °C). The data were checked for thermodynamic consistency by using the Redlich–Kister area test. The interaction parameters of the various models for the excess Gibbs energy were fitted to the measured data, which were also used to determine the C=C/CHO and CHO/CCOO interaction parameters for the UNIFAC method. These parameters are, for example, required for the prior calculation of the vapor–liquid equilibrium behavior of crotonaldehyde systems.

Introduction

One of the most important methods for calculating vapor–liquid equilibria is the group contribution method UNIFAC (*1*). Apart from the values of the data for the pure substances, such as the van der Waals volumes R_k and van der Waals surface areas Q_k of the structural groups, this model requires only the group interaction parameters a_{mn}. These parameters can be obtained from experimental data: vapor–liquid (VLE) and liquid–liquid equilibrium (LLE) data as well as activity coefficients at infinite dilution can be used. The majority of the previously published VLE data are stored in the Dortmund Data Bank and were used for fitting the UNIFAC parameters. However, the UNIFAC parameter table is incomplete, so that further experimental vapor–liquid equilibrium measurements are necessary to increase the scope of this method. Systems which could not be satisfactorily measured by using the conventional dynamic and static methods of measurement are of particular interest. "Not satisfactorily" means that the data do not pass a test for thermodynamic consistency, so that they are not suitable for fitting the group interaction parameters. Such systems are, for example, aldehyde–alkene and to some extent aldehyde–ester systems. The subject of this investigation was to test the headspace gas chromatography (*2*, *3*) for measuring vapor–liquid equilibria. This technique permits the measurement of various different systems and can be carried out much more simply than the static and dynamic methods of measurement. Thus, investigation of aldehyde–alkene and aldehyde–ester systems made it possible to determine the parameters for interaction between the CHO group and the C=C and the CCOO groups and thereby to fill out further gaps in the UNIFAC parameter table. These parameters are, for example, required for calculations on systems containing components such as crotonaldehyde in the construction of vinyl acetate plants.

Purification of the Substances

All chemicals used were commercial samples. The purification of the substances was carried out by rectification using a packed column. The purity was checked by means of gas chromatography and was in each case ca. 99.9%. Table I contains a list of the suppliers of the substances used for the measurements.

Table I

component	supplier
ethanol	Merck AG
1-propanol	Merck AG
toluene	Merck AG
n-decane	Merck-Schuchardt
1-hexene	EGA Chemie
1-octene	Merck-Schuchardt
1-decene	Merck AG
valeraldehyde	Ruhrchemie AG
butyraldehyde	Riedel de Haen AG
ethyl acetate	Riedel de Haen AG
butyl acetate	Merck AG

Table II

system	temp, °C	stat. phase
ethanol–toluene	45.4	Carbowax 20 M on Chromosorb 750
1-propanol–*n*-decane	93.0	squalane on Chromosorb W
valeraldehyde–1-octene	81.8	squalane on Chromosorb W
1-hexene–valeraldehyde	40.3	squalane on Chromosorb W
butyraldehyde–1-octene	55.4	squalane on Chromosorb W
valeraldehyde–1-decene	80.3	squalane on Chromosorb W
ethyl acetate–valeraldehyde	49.3	OV1 on Chromosorb G
valeraldehyde–butyl acetate	80.4	OV1 on Chromosorb G
butyraldehyde–butyl acetate	52.8	OV351 on Chromosorb 750

Table III. Experimental Data and Fitted Parameters for the System Ethanol (1)–Toluene (2) at 45.4 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	2.190	1.642		0.0201
Van Laar	2.192	1.641		0.0171
Wilson	1360	304.3		0.0098
NRTL	430.5	1036	0.2895	0.0151
UNIQUAC	−121.8	823.2		0.0142

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0076	0.1338	0.2983	0.6334	0.6913	0.7278
0.0340	0.3880	0.3545	0.6363	0.7169	0.7406
0.0412	0.4071	0.4072	0.6542	0.7377	0.7482
0.0629	0.5068	0.4519	0.6741	0.8054	0.7703
0.0748	0.5264	0.5083	0.6768	0.8555	0.7993
0.1021	0.5508	0.5542	0.6908	0.9058	0.8446
0.1478	0.5838	0.6049	0.7064	0.9591	0.9111
0.1957	0.6008	0.6532	0.7181	0.9870	0.9589
0.2527	0.6209	0.6712	0.7222		

Apparatus

The experimental setup consisted of an F 22 gas chromatograph in combination with a Perkin-Elmer F 45 GLC vapor analyzer. The F 22 gas chromatograph is a conventional instrument for two-channel operation. When the F 45 vapor analyzer is used, one channel is reserved for the vapor-phase

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Table IV. Experimental Data and Fitted Parameters for the System 1-Propanol (1)–*n*-Decane (2) at 93.0 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	1.555	2.137		0.0100
Van Laar	1.564	2.181		0.0098
Wilson	1270	519.0		0.0097
NRTL	1262	385.1	0.2932	0.0096
UNIQUAC	−98.23	646.0		0.0097

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0127	0.3644	0.2739	0.9067	0.6895	0.9311
0.0159	0.5321	0.3796	0.9138	0.7420	0.9371
0.0345	0.6546	0.4265	0.9160	0.8143	0.9436
0.0539	0.7485	0.4812	0.9221	0.8460	0.9487
0.0631	0.7626	0.5368	0.9279	0.8679	0.9499
0.1261	0.8605	0.5907	0.9280	0.9176	0.9607
0.1831	0.8814	0.6229	0.9289	0.9567	0.9725
0.2351	0.8939	0.6520	0.9320	0.9888	0.9923

Table V. Experimental Data and Fitted Parameters for the System Valeraldehyde (1)–1-Octene (2) at 81.8 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.7710	0.5264		0.0072
Van Laar	0.7880	0.5350		0.0068
Wilson	854.5	−293.2		0.0066
NRTL	−151.5	715.2	0.2995	0.0068
UNIQUAC	−270.8	501.1		0.0070
UNIFAC				0.0060

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0293	0.1208	0.2409	0.4356	0.6935	0.7506
0.0467	0.1514	0.2939	0.4708	0.7433	0.7841
0.0622	0.1833	0.3388	0.5149	0.7929	0.8211
0.0853	0.2144	0.3942	0.5640	0.9015	0.9101
0.1087	0.2540	0.4468	0.6008	0.9174	0.9212
0.1258	0.2873	0.4915	0.6311	0.9390	0.9434
0.1437	0.3182	0.5397	0.6615	0.9575	0.9621
0.1649	0.3435	0.5891	0.6889	0.9778	0.9784
0.1856	0.3735	0.6402	0.7202		

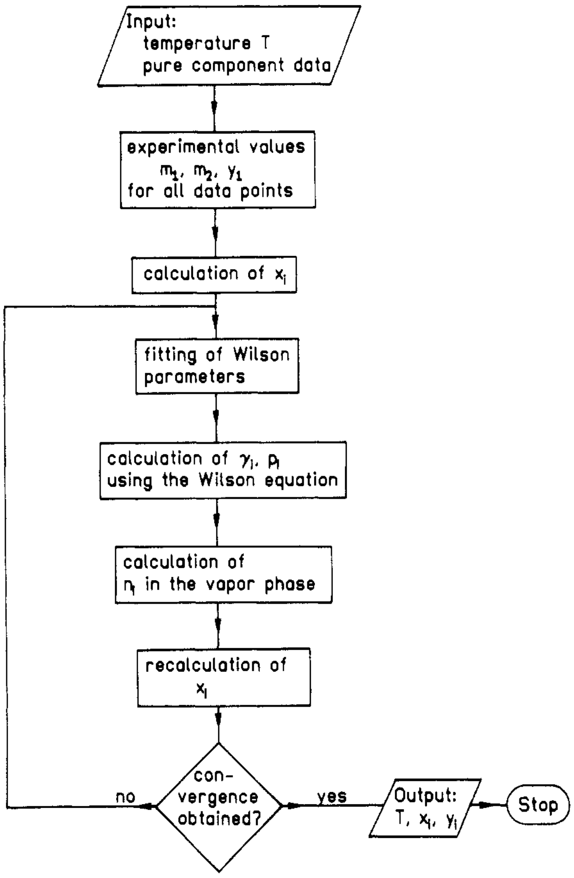

Figure 1. Flow diagram for the recalculation of the liquid-phase composition.

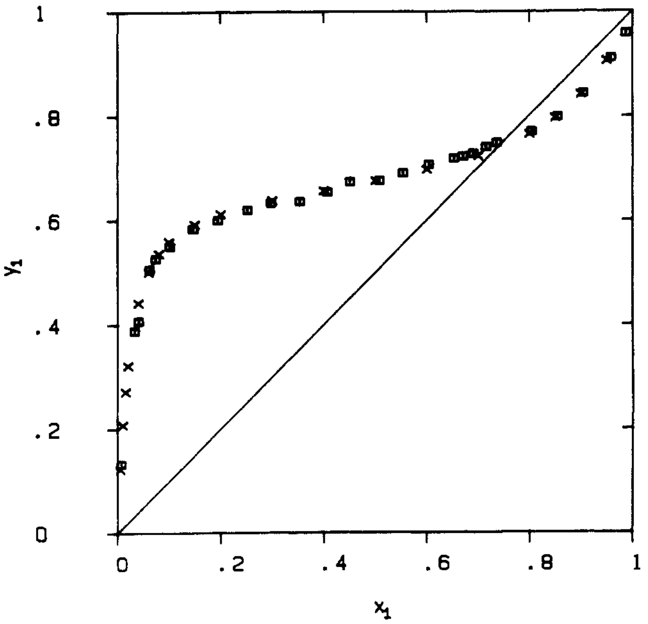

Figure 2. y–x diagram for the system ethanol (1)–toluene (2): (□) data from headspace gas chromatography at 45.4 °C; (×) data from van Ness et al. (*10*) at 45.0 °C.

samples, while liquid samples can be analyzed in a conventional manner using the second injection block. The liquid samples for vapor-phase analysis were mixed in known ratios in glass vials, the volume of which is ca. 22 mL. The amounts of substance used were ca. 2–3 mL. The sample vials were tightly closed by means of a special aluminum lid, underneath which was a washer and a silicone disk coated with aluminum. The vials were kept in a thermostated aluminum block, the temperature of which could be adjusted between 35 and 150 °C. Samples were removed from the vapor phase above the liquid by means of an electropneumatic dosage system. This consists of a dosage needle which is separated from the atmosphere by a movable cylinder. The sample vial is situated axially below the dosage needle in the thermostated aluminum block. To obtain a sample, the aluminum block containing the vials rises vertically and thus shifts the movable cylinder. The dosage needle pierces the rubber seal of this cylinder and of the sample vial and enters the vapor phase inside the vial. The dosage needle is connected directly with the carrier gas introduction system and is thus under the prevailing carrier gas pressure. Carrier gas now flows into the sample vial via the dosage needle until the former is also filled at the carrier gas pressure. After the pressure has been built up in this manner, a magnetic valve stops the flow of carrier gas and the compressed gas in the sample vial expands via the dosage needle into the chromatography column; i.e., the gas and the components to be measured flow together onto the column. The dosage is stopped by opening the magnetic valve. The analysis time can be chosen to be anywhere between 0.1 and 99 min. Digital switches are used to set the analysis time and the temperatures of the oven, injector port, and detector. The sample changer can take up to 30 sample vials. Detectors of various types can be used. The measurements to be discussed below were carried out by using a thermal conductivity detector for

Table VI. Experimental Data and Fitted Parameters for the System 1-Hexene (1)–Valeraldehyde (2) at 40.3 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.7071	0.7350		0.0044
Van Laar	0.7072	0.7351		0.0044
Wilson	105.9	391.9		0.0042
NRTL	278.7	196.9	0.3006	0.0043
UNIQUAC	132.7	1.339		0.0044
UNIFAC				0.0076

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0086	0.0752	0.3563	0.7646	0.7244	0.9008
0.0306	0.2231	0.3879	0.7779	0.7851	0.9158
0.0600	0.3408	0.4082	0.7898	0.8187	0.9265
0.0776	0.4124	0.4480	0.8052	0.8455	0.9426
0.1448	0.5456	0.4776	0.8169	0.8779	0.9484
0.1608	0.5897	0.5086	0.8278	0.9063	0.9600
0.1794	0.6049	0.5685	0.8537	0.9426	0.9731
0.2379	0.6637	0.6029	0.8602	0.9681	0.9825
0.2961	0.7251	0.6610	0.8770		

Table VII. Experimental Data and Fitted Parameters for the System Butyraldehyde (1)–1-Octene (2) at 55.4 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.6800	0.7184		0.0038
Van Laar	0.6801	0.7199		0.0037
Wilson	573.9	−63.53		0.0036
NRTL	314.3	171.9	0.2980	0.0037
UNIQUAC	−149.7	347.0		0.0038
UNIFAC				0.0100

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0199	0.1815	0.2690	0.7323	0.7439	0.9170
0.0622	0.3812	0.3150	0.7569	0.8092	0.9357
0.0773	0.4204	0.3684	0.7842	0.8378	0.9446
0.1008	0.4875	0.4524	0.8189	0.8670	0.9510
0.1191	0.5454	0.5280	0.8528	0.9075	0.9639
0.1381	0.5736	0.5657	0.8598	0.9322	0.9734
0.1581	0.6145	0.5924	0.8721	0.9563	0.9821
0.1976	0.6541	0.6239	0.8826	0.9945	0.9978
0.2299	0.6897	0.6856	0.8975	0.9947	0.9979

Table VIII. Experimental Data and Fitted Parameters for the System Valeraldehyde (1)–1-Decene (2) at 80.3 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.5496	0.5148		0.0032
Van Laar	0.5498	0.5156		0.0032
Wilson	604.6	−190.8		0.0034
NRTL	196.3	202.7	0.3003	0.0034
UNIQUAC	−225.7	403.7		0.0032
UNIFAC				0.0104

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0109	0.1640	0.2024	0.7796	0.6524	0.9435
0.0339	0.3966	0.2532	0.8171	0.7029	0.9511
0.0399	0.4279	0.2919	0.8370	0.7496	0.9596
0.0635	0.5331	0.3421	0.8643	0.8046	0.9700
0.0638	0.5332	0.4015	0.8824	0.8513	0.9746
0.0815	0.5912	0.4506	0.8976	0.8980	0.9818
0.1028	0.6519	0.5465	0.9254	0.9508	0.9911
0.1450	0.7150	0.5983	0.9343		

Table IX. Experimental Data and Fitted Parameters for the System Ethyl Acetate (1)–Valeraldehyde (2) at 49.3 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.0643	0.0598		0.0034
Van Laar	0.0643	0.0600		0.0034
Wilson	114.3	−72.69		0.0034
NRTL	−51.43	93.88	0.2984	0.0034
UNIQUAC	−78.00	96.34		0.0034
UNIFAC				0.0150

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0416	0.1041	0.3501	0.5714	0.6457	0.8230
0.1022	0.2359	0.3988	0.6249	0.6997	0.8577
0.1482	0.3146	0.4474	0.6730	0.7502	0.8864
0.1957	0.3997	0.4990	0.7147	0.7968	0.9073
0.2459	0.4607	0.5450	0.7573	0.8459	0.9327
0.2960	0.5211	0.5946	0.7864	0.9063	0.9568

Table X. Experimental Data and Fitted Parameters for the System Valeraldehyde (1)–Butyl Acetate (2) at 80.4 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	0.0513	0.1238		0.0038
Van Laar	0.0635	0.0996		0.0041
Wilson	−48.73	150.8		0.0041
NRTL	391.8	−283.3	0.3234	0.0041
UNIQUAC	122.8	−95.51		0.0041
UNIFAC				0.0103

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0422	0.0901	0.3932	0.6067	0.7176	0.8456
0.0739	0.1639	0.4364	0.6457	0.7597	0.8718
0.1187	0.2403	0.4780	0.6809	0.7972	0.8933
0.1657	0.3203	0.5205	0.7077	0.8466	0.9243
0.1911	0.3602	0.5606	0.7395	0.8822	0.9408
0.2312	0.4217	0.6007	0.7698	0.9185	0.9652
0.2775	0.4776	0.6394	0.8038	0.9595	0.9820
0.3213	0.5302	0.6795	0.8283	0.9673	0.9852
0.3570	0.5593				

Table XI. Experimental Data and Fitted Parameters for the System Butyraldehyde (1)–Butyl Acetate (2) at 52.8 °C

constant	A_{12}	A_{21}	α_{12}	mean devn in y
Margules	−0.0201	−0.0380		0.0042
Wilson	141.8	−145.7		0.0044
NRTL	112.6	−120.6	0.3183	0.0044
UNIQUAC	−174.2	210.5		0.0042
UNIFAC				0.0177

Experimental Data

x_1	y_1	x_1	y_1	x_1	y_1
0.0450	0.2473	0.3164	0.7646	0.6136	0.9209
0.0634	0.3184	0.3539	0.7901	0.6546	0.9236
0.0933	0.4194	0.3871	0.8159	0.6931	0.9346
0.1329	0.5145	0.4188	0.8416	0.6978	0.9351
0.1538	0.5605	0.4563	0.8494	0.7341	0.9514
0.1897	0.6211	0.4907	0.8656	0.8144	0.9672
0.2313	0.6932	0.5246	0.8813	0.8969	0.9832
0.2563	0.7060	0.5465	0.8842	0.9505	0.9917
0.2852	0.7292	0.5871	0.9015		

the determination of the composition of the vapor phase. Integration of the peak areas was carried out by a Hewlett-Packard HP 3390 A integrator, which also recorded the retention times; it permits the recording of the complete gas chromatogram.

Before the measurements were carried out, modifications of the apparatus were performed in cooperation with Bayer AG in Leverkusen. An additional device for the injection of liquid samples was built into the channel for vapor-phase analysis: it functions via a type of bypass. The manufacturer had originally intended the second channel of the chromatograph to be used for the injection of liquid samples; however, it became

Table XII. Pure-Component Properties

component i	v_i, mL/mol	r_i	q_i
ethanol	58.69	2.1055	1.9720
1-propanol	75.14	2.7799	2.5120
toluene	106.85	3.9228	2.9680
n-decane	195.92	7.1974	6.0160
1-hexene	125.90	4.2697	3.6440
1-octene	157.86	5.6185	4.7240
1-decene	190.35	6.9673	5.8040
butyraldehyde	88.27	3.2479	2.8760
valeraldehyde	106.41	3.9223	3.4160
ethyl acetate	98.49	3.4786	3.1160
butyl acetate	132.55	4.8274	4.1960

clear in the course of investigations carried out by the Bayer AG that it is imperative to carry out the measurements on the same column which has been used for calibration, since it is not possible to construct an exact copy of the column for vapor-phase analysis and to situate this in the second channel.

Initial difficulties were also experienced when systems with widely differing volatilities were measured, due to condensation effects in the sampling system. The dosage needle was thus coated with silver to increase its thermal conductivity. Devices for heating the dosage space and the carrier gas were also installed. Heat transfer in the thermostat was improved by filling the aluminum block with silicone oil. An aluminum ring which increased the stability of the sample vials in the thermostat was constructed and screwed onto the aluminum block. The bath temperature of the thermostat was measured by using an iron-constantan thermoelement; temperature display was carried out by a Fluke 2170 A digital thermometer. The chromatographic columns were made of glass and were 2 m long with external diameter $^1/_4$ in.

Measurements and Their Interpretation

Samples were weighed directly into the sample vials by using an analytical balance, the accuracy of which was ±0.1 mg. The amounts of samples were between 2 and 3 mL. After the vials had been closed as described above, they were brought to the appropriate temperature in the thermostat. Measurements were commenced after equilibrium had been reached. Optimum values for the apparative parameters oven, injector, and detector temperature as well as for injection and analysis times were obtained in prior experiments. The stationary phases were chosen so that the peaks were completely separated from each other and, since a thermal conductivity detector was used, from the peak due to air. The measurements were carried out automatically, the integrator being switched on at the beginning of the injection and off at the end of the analysis period. The analysis protocol containing the peak areas was then printed out and the next sample subjected to the measurement procedure.

Calibration was necessary before the peak areas could be used to determine the composition of the vapor phase. This was carried out by preparing about 10 samples of differing composition, the relative concentrations being chosen according to the vapor concentrations expected in the actual measurements. Then, for the calibrations, liquid samples (0.3-0.5 μL, depending on the system) were transferred to the column via the additional injector port by means of a syringe. The calibration curve was obtained by plotting the percent peak area for one of the components against the molar concentration of this component in the calibration mixtures. This curve could then be used to convert the peak areas obtained from the vapor-phase analysis into the molar concentration of the relevant component in the vapor phase as a function of the liquid composition.

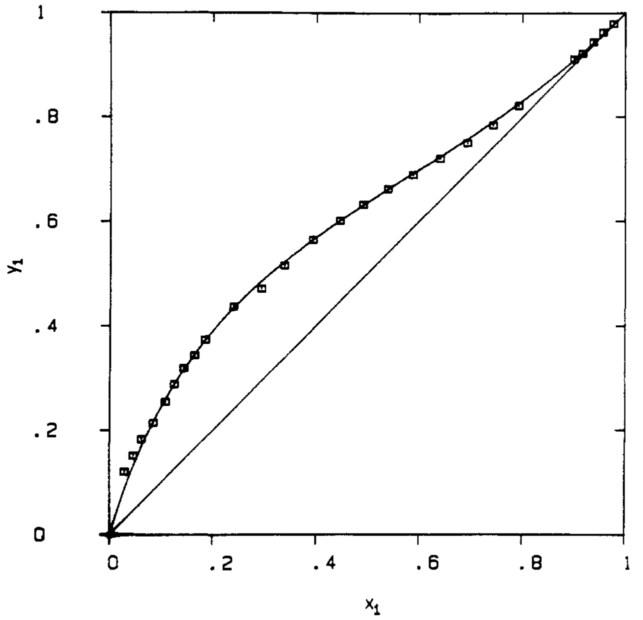

Figure 3. y-x diagram for the system valeraldehyde (1)-1-octene (2) at 81.8 °C.

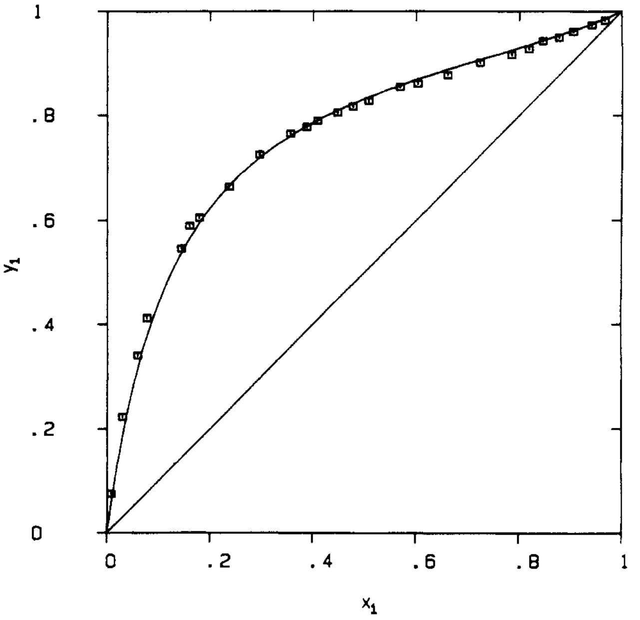

Figure 4. y-x diagram for the system 1-hexene (1)-valeraldehyde (2) at 40.3 °C.

This procedure was simplified and errors arising from plotting the calibration curve and reading off the values were avoided by using a computer to analyze the data. To this end, the calibration curve is represented by a polynomial, the coefficients of which are fitted to the calibration values by linear regression analysis. The computer program calculates the composition of the vapor phase from the peak areas with the help of the polynomial. It was necessary to take into consideration that the liquid composition determined from the amounts weighed out did not correspond to the equilibrium composition at the relevant temperature of measurement. The composition of the liquid phase varies as a function of the volatilities of the components of the system. The procedure used by the program to correct the liquid concentrations is shown in the flow diagram (Figure 1). Since the pressure cannot be measured, the correction of the rough y-x data is carried out by iteration whereby the volume of the vapor phase is calculated by

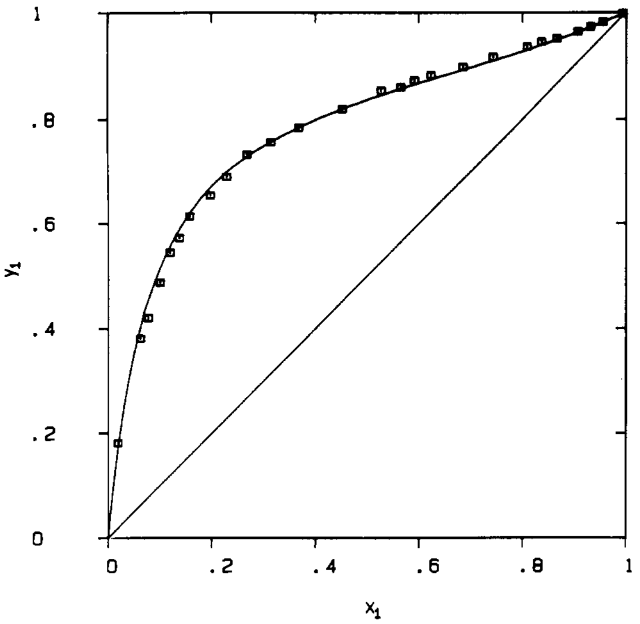

Figure 5. y–x diagram for the system butyraldehyde (1)–1-octene (2) at 55.4 °C.

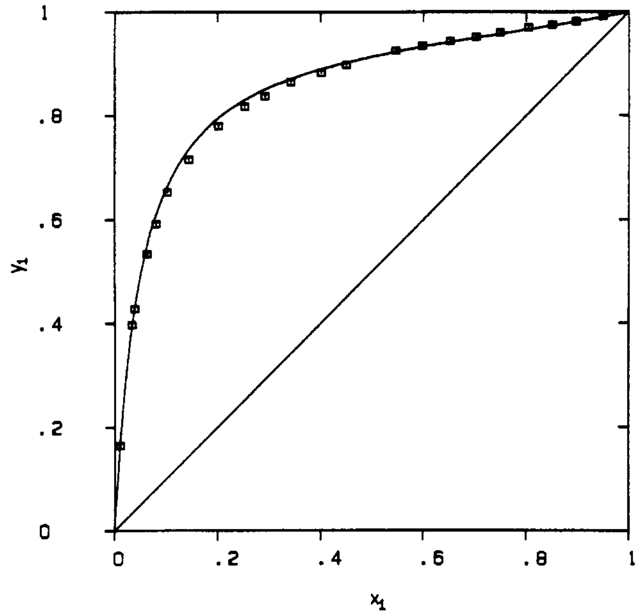

Figure 6. y–x diagram for the system valeraldehyde (1)–1-decene (2) at 80.3 °C.

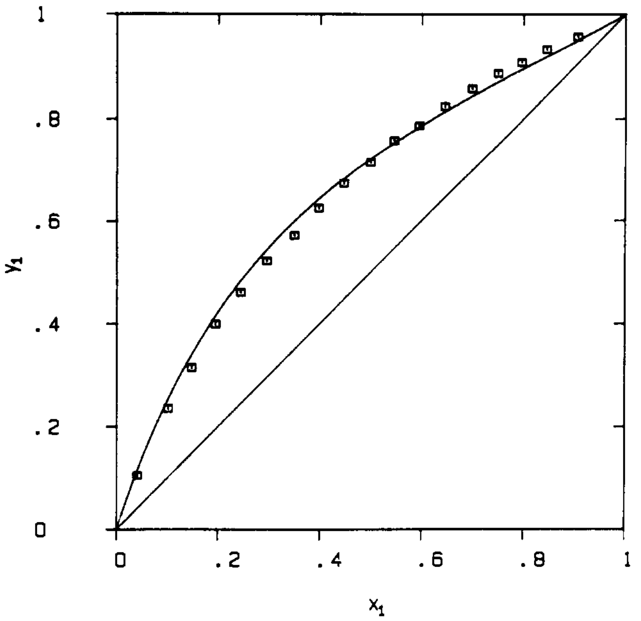

Figure 7. y–x diagram for the system ethyl acetate (1)–valeraldehyde (2) at 49.3 °C.

knowing the total volume of the vial, the mass, and the density of the liquid mixture. The thermodynamic consistency of the corrected data obtained in this way was checked with the help of the Redlich–Kister area test (*4*). The total pressure is not required for this test, since it cancels out when the ratios of the activity coefficients are calculated. The data were considered to be thermodynamically consistent when the area deviation was less than 10%. If the system considered was almost ideal, i.e., all activity coefficients lay between 0.95 and 1.10, the test was not carried out.

Results

The nine systems investigated, together with the relevant temperatures of measurement and the stationary phases used for the chromatographic separation, are listed in Table II. The experimental data and the fitted parameters for the Margules (*5*), van Laar (*6*), Wilson (*7*), NRTL (*8*), and UNIQUAC (*9*) equations are to be found in Tables III–XI. These also contain the mean deviations of the mole fractions in the vapor phase calculated by using the various models. The following function was used in fitting the parameters:

$$F = \sum_{i}^{\mathrm{NDP}} \sum_{j}^{\mathrm{NC}} |(y_i/x_i)_{\mathrm{exptl}} - (y_i/x_i)_{\mathrm{calcd}}|$$

where NDP is the number of data points and NC is the number of components. It was assumed for the fitting procedure that the vapor phases behaved ideally.

For the models which are based on the concept of local composition the following relations are valid for the parameter A_{ij} in Tables III–XI:

Wilson

$$A_{ij} = (\lambda_{ij} - \lambda_{ii}) \text{ in cal/mol}$$

NRTL

$$A_{ij} = (g_{ij} - g_{jj}) \text{ in cal/mol}$$

UNIQUAC

$$A_{ij} = (u_{ij} - u_{jj}) \text{ in cal/mol}$$

The parameters of the pure compounds, which are required for calculations using the Wilson and UNIQUAC equations, can be found in Table XII.

Measurements using the test systems ethanol–toluene and 1-propanol–n-decane were carried out to examine the suitability of headspace gas chromatography for studying vapor–liquid equilibria. A comparison of our results with those reported by Van Ness et al. (*10*) and Ellis et al. (*11*) showed the agreement to be very good, although these authors had carried out their measurements by using considerably more complicated static and dynamic procedures, respectively. As an example, Figure 2 shows a comparison between the x–y data of the ethanol–toluene system reported by Van Ness (*10*) and our data. The aldehyde–alkene systems show positive deviations from Raoult's law, the activity coefficients in the liquid phase lying between 1 and ca. 2.4. In contrast, the aldehyde–ester systems behave in an almost ideal manner, the corresponding

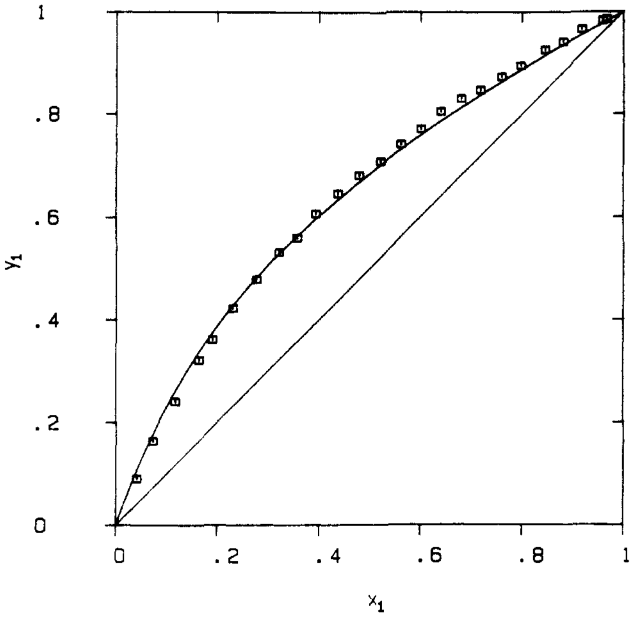

Figure 8. *y*–*x* diagram for the system valeraldehyde (1)–butyl acetate (2) at 80.4 °C.

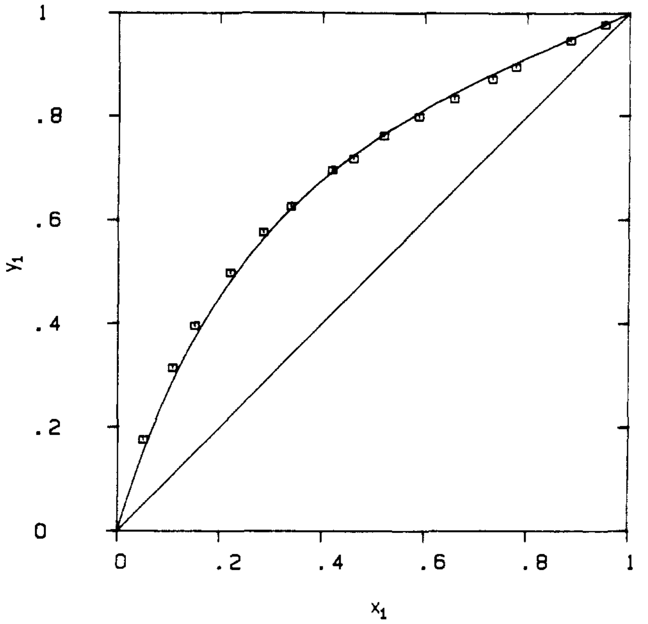

Figure 10. *y*–*x* diagram for the system vinyl acetate (1)–crotonaldehyde (2) at 40.0 °C; experimental data from Waradzin et al. (*12*).

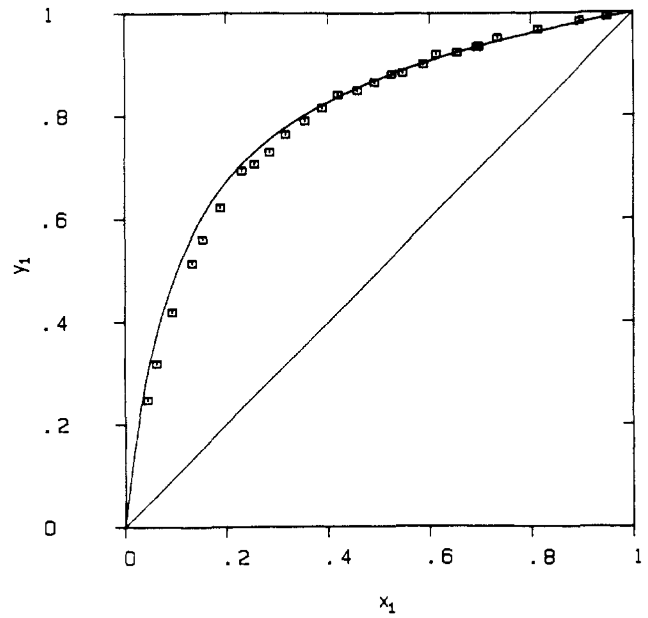

Figure 9. *y*–*x* diagram for the system butyraldehyde (1)–butyl acetate (2) at 52.8 °C.

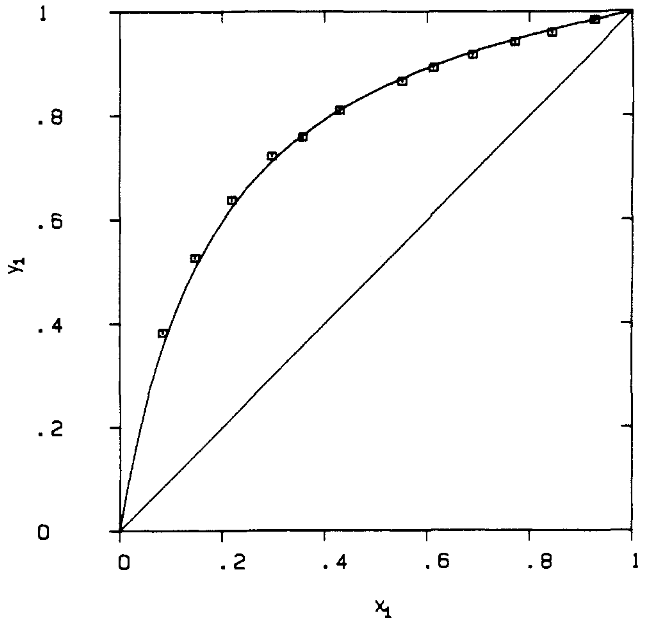

Figure 11. *y*–*x* diagram for the system acetone (1)–crotonaldehyde (2) at 40.0 °C; experimental data from Waradzin et al. (*12*).

activity coefficients having values between 1 and 1.08 (i.e., there is a slight positive deviation from Raoult's law). The measured VLE data of the aldehyde–alkene and aldehyde–ester systems were used to obtain new UNIFAC interaction parameters. Data reported by Waradzin et al. (*12*), Pesterova et al. (*13*), and Mühlenbruch et al. (*14*) were also taken into account in fitting the interaction parameters between the CHO and CCOO groups. The following new UNIFAC parameters were determined: $a_{C=C,CHO}$ = 448.8 K, $a_{CHO,C=C}$ = 56.30 K, $a_{CHO,CCOO}$ = −162.6 K, $a_{CCOO,CHO}$ = 400.9 K. All other group interaction parameters used in the calculations were taken from ref *15* and *16*.

The mean deviations of the mole fractions in the vapor phase calculated by the UNIFAC method with these parameters are also given in Tables V–XI for the various systems. Figures 3–9 show the *x*–*y* diagrams for the four measured aldehyde–alkene and the three aldehyde–ester systems. The experimental data are denoted by the symbol □, while the continuous line shows the values calculated by using the UNIFAC method. In all cases the agreement between experimental and calculated values is good. The newly determined UNIFAC parameters for interaction between the aldehyde and alkene or aldehyde and ester groups can also be used to calculate the vapor–liquid behavior of other systems, such as, for example, those involved in the industrial preparation of vinyl acetate. Figures 10–12 show the *x*–*y* diagram for the systems vinyl acetate–crotonaldehyde, acetone–crotonaldehyde, and water–crotonaldehyde. Experimental data are again denoted by the symbol □, while the continuous line shows the values calculated according to UNIFAC. The system water–crotonaldehyde exhibits a miscibility gap which is reproduced fairly well by the UNIFAC equation.

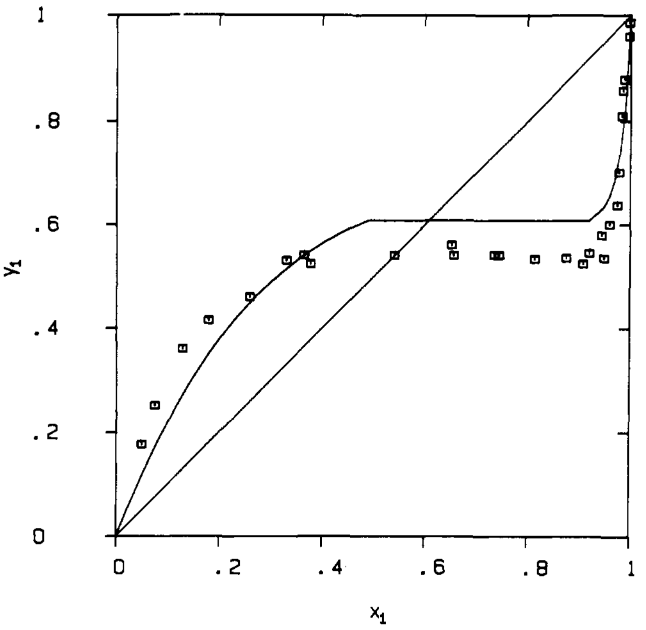

Figure 12. y–x diagram for the system water (1)–crotonaldehyde (2) at 760 mmHg; experimental data from Kil et al. (*17*).

Conclusion

The technique of gas-chromatographic vapor-phase analysis permits the determination of vapor–liquid equilibrium data for widely varying systems using a simple experimental setup. It is thus possible to extend in a short time the data base for fitting new UNIFAC interaction parameters. The small selection of examples discussed here show that, with the help of only four new UNIFAC parameters, vapor–liquid equilibrium data for a large number of further systems can be predicted. This is the great advantage of the group concept on which the UNIFAC method is based.

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Glossary

A_{ij}	parameters used in the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equation
a_{mn}	interaction parameter in the UNIFAC equation
F	objective function
g_{ij}	interaction parameter in the NRTL equation
m_i	mass of component i
NC	number of components
NDP	number of data points
n_i	mole number of component i
p_i	partial pressure of component i
Q_k	relative van der Waals surface area of group k
q_i	relative van der Waals surface area of component i
R_k	relative van der Waals volume of group k
r_i	relative van der Waals volume of component i
T	temperature
u_{ij}	interaction parameter in the UNIQUAC equation
v_i	liquid molar volume of component i
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

Greek Letters

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

Subscripts

exptl	experimental
calcd	calculated

Registry No. Ethanol, 64-17-5; toluene, 108-88-3; 1-propanol, 71-23-8; n-decane, 124-18-5; valeraldehyde, 110-62-3; 1-octene, 111-66-0; 1-hexene, 592-41-6; 1-decene, 872-05-9; ethyl acetate, 141-78-6; butyl acetate, 123-86-4; butyraldehyde, 123-72-8.

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