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Extension of Unifac by Headspace Gas Chromatography. 2

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Isothermal vapor–liquid equilibrium data for the following binary systems have been obtained by means of headspace gas chromatography: valeraldehyde–toluene (70.1 °C), isobutyraldehyde–benzene (39.2 °C), isobutyraldehyde–toluene (40.4 °C), *n*-butyraldehyde–benzene (35.2 °C), *tert*-butyl alcohol–*n*-heptane (60.1 °C), *tert*-butyl alcohol–*n*-octane (65.3 °C), *tert*-butyl alcohol–*n*-decane (70.1 °C), and valeraldehyde–toluene–1-octene (44.7 °C). The interaction parameters for different g^E models were fitted by using the experimental data. The data for aldehyde–aromatic systems were also used to determine the ACH/CHO and $ACCH_2$/CHO interaction parameters for the Unifac method.

Introduction

We showed in an earlier publication (*1*) that headspace gas chromatographic analysis is suitable for measuring vapor–liquid equilibria in many different systems. This method permits the isothermal determination of the vapor concentration as a function of that of the liquid. Because of the shorter measurement times, the method is particularly suited for the study of mixtures whose components can chemically react either with themselves or with other compounds present in the mixture. Apart from the rapid determination of data which are directly required for the purposes of process technology, it is in addition also possible to enlarge the data basis for the fitting of new interaction parameters for the group contribution method Unifac (*2*) in a very short time. The purpose of the studies reported here was to determine vapor–liquid equilibrium data for binary systems containing aldehydes and aromatics. These data then made possible the calculation of Unifac interaction parameters between the –CHO and the –ACH or $-ACCH_2$ groups and thus to fill two further gaps in the parameter matrix of the Unifac method.

We have also studied three alkane/*tert*-butyl alcohol systems. These investigations are of interest from three points of view. *tert*-Butyl alcohol is an important intermediate in the chemical industry: it is obtained by hydrolysis of isobutylene and, after subsequent cleavage, makes possible the selective removal of isobutylene from the C_4 fraction. Isobutene itself is the startup material for various polymerization products. These data are also of interest from the point of view of the further development of the Unifac method. In order to make possible a better description of the vapor–liquid behavior of systems containing secondary and tertiary alcohols, separate van der Waals volume and surface parameters for the primary, secondary, and tertiary alcohol groups were introduced in a modified Unifac approach. Preliminary results obtained by using the modified Unifac method have been published (*3*, *4*).

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
benzene	Merck AG
toluene	Merck AG
n-butyraldehyde	Riedel de Haen AG
isobutyraldehyde	Riedel de Haen AG
valeraldehyde	Ruhrchemie AG
n-heptane	Merck AG
n-octane	Merck AG
n-decane	Merck-Schuchardt
tert-butyl alcohol	Merck AG

Table II

system	temp, °C	stat. phase
valeraldehyde–toluene	70.1	OV1 on Chromosorb G
isobutyraldehyde–benzene	39.2	OV351 on Chromosorb 750
isobutyraldehyde–toluene	40.4	Carbowax 20 M on Chromosorb 750
n-butyraldehyde–benzene	35.2	squalane on Chromosorb W
n-heptane–*tert*-butyl alcohol	60.1	squalane on Chromosorb W
n-octane–*tert*-butyl alcohol	65.3	squalane on Chromosorb W
tert-butyl alcohol–*n*-decane	70.1	squalane on Chromosorb W
valeraldehyde–toluene–1-octene	44.7	OV1 on Chromosorb G

Table III. Experimental Data and Fitted Parameters for the System Valeraldehyde (1)–Toluene (2) at 70.1 °C

constants	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.0695	0.1690		0.0062
Van Laar	0.0740	0.2471		0.0058
Wilson	−341.5	586.4		0.0060
NRTL	679.8	−453.8	0.3010	0.0062
Uniquac	534.8	−388.2		0.0060
Unifac				0.0092

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0286	0.0377	0.2001	0.2565	0.4884	0.5527	0.7736	0.8123
0.0607	0.0765	0.2409	0.3033	0.5212	0.5830	0.8112	0.8463
0.0820	0.1062	0.2894	0.3531	0.5683	0.6274	0.8925	0.9120
0.0993	0.1320	0.3268	0.3955	0.6112	0.6679	0.9117	0.9281
0.1393	0.1771	0.3657	0.4333	0.6500	0.7019	0.9320	0.9449
0.1419	0.1826	0.4036	0.4667	0.6871	0.7371	0.9682	0.9768
0.1681	0.2161	0.4458	0.5098	0.7237	0.7709		

Apparatus and Measurements

The experimental setup consisted of an F22 gas chromatograph connected to a Perkin-Elmer F45 GLC vapor analyzer as described in ref *1*. The binary measurements were carried out and evaluated in a manner analogous to that described in ref *1*. The data fulfil the requirements of the Redlich–Kister area test (*5*) and can thus be considered to be thermodynamically consistent. The gas chromatographic headspace analysis can

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Table IV. Experimental Data and Fitted Parameters for the System Isobutyraldehyde (1)–Benzene (2) at 39.2 °C

constants	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.0936	0.1315		0.0061
Van Laar	0.0914	0.1377		0.0059
Wilson	−180.1	289.9		0.0059
NRTL	334.9	−225.7	0.3032	0.0060
Uniquac	−100.3	96.51		0.0065
Unifac				0.0072

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0617	0.1261	0.1999	0.3141	0.4489	0.5990	0.8087	0.8775
0.0809	0.1557	0.2304	0.3394	0.4918	0.6331	0.8525	0.9050
0.1019	0.1801	0.2877	0.4234	0.6040	0.7254	0.8915	0.9292
0.1124	0.1902	0.3118	0.4360	0.6511	0.7653	0.9103	0.9420
0.1414	0.2428	0.3710	0.5241	0.6930	0.7931	0.9272	0.9492
0.1678	0.2573	0.4087	0.5677	0.7733	0.8504	0.9624	0.9723

Table V. Experimental Data and Fitted Parameters for the System Isobutyraldehyde (1)–Toluene (2) at 40.4 °C

constants	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.3775	0.2497		0.0048
Van Laar	0.3823	0.2572		0.0046
Wilson	463.7	−213.8		0.0046
NRTL	−237.0	502.8	0.2991	0.0046
Uniquac	−262.3	377.3		0.0044
Unifac				0.0108

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0446	0.2609	0.1560	0.5490	0.3924	0.7862	0.6367	0.9058
0.0539	0.2853	0.1921	0.6088	0.4325	0.7950	0.7161	0.9239
0.0763	0.3802	0.2334	0.6566	0.4757	0.8329	0.8000	0.9492
0.0989	0.4375	0.2776	0.6800	0.5167	0.8529	0.8420	0.9595
0.1126	0.4758	0.3085	0.7286	0.5584	0.8720	0.9028	0.9768
0.1324	0.5151	0.3504	0.7670	0.5969	0.8838	0.9393	0.9849
						0.9605	0.9898

Table VI. Experimental Data and Fitted Parameters for the System *n*-Butyraldehyde (1)–Benzene (2) at 35.2 °C

constants	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	0.0821	0.0250		0.0025
Van Laar	0.0995	0.0311		0.0025
Wilson	427.2	−293.7		0.0025
NRTL	−383.6	515.1	0.2991	0.0025
Uniquac	180.7	−181.1		0.0022
Unifac				0.0039

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0438	0.0553	0.2368	0.2772	0.5125	0.5532	0.8065	0.8304
0.0719	0.0885	0.2768	0.3156	0.5585	0.5970	0.8419	0.8616
0.0926	0.1134	0.3092	0.3504	0.5955	0.6334	0.8789	0.8939
0.1010	0.1222	0.3487	0.3922	0.6352	0.6723	0.9027	0.9145
0.1346	0.1629	0.3832	0.4217	0.6779	0.7108	0.9248	0.9336
0.1556	0.1863	0.4358	0.4771	0.7176	0.7494	0.9541	0.9615
0.1959	0.2317	0.4699	0.5090	0.7597	0.7866	0.9836	0.9873

Table VII. Experimental Data and Fitted Parameters for the System *tert*-Butyl Alcohol (1)–*n*-Heptane (2) at 60.1 °C

constants	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	1.791	1.058		0.0141
Van Laar	1.849	1.097		0.0093
Wilson	1397	−60.51		0.0072
NRTL	402.0	1024	0.6305	0.0065
Uniquac	−273.5	738.0		0.0097
Unifac				0.0429

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0611	0.2795	0.2280	0.4442	0.6203	0.5983	0.8505	0.7673
0.0665	0.3011	0.2688	0.4473	0.6702	0.6315	0.8893	0.8052
0.0831	0.3300	0.3303	0.4782	0.7170	0.6589	0.9228	0.8555
0.1124	0.3550	0.3656	0.4888	0.7616	0.6900	0.9527	0.8933
0.1384	0.3949	0.4107	0.5069	0.7945	0.7164	0.9723	0.9332
0.1450	0.3886	0.4598	0.5230	0.8121	0.7327	0.9819	0.9653
0.1815	0.4064	0.4938	0.5473				

Table VIII. Experimental Data and Fitted Parameters for the System *tert*-Butyl Alcohol (1)–*n*-Octane (2) at 65.3 °C

constants	A_{12}	A_{21}	α_{21}	mean dev in y
Margules	1.639	0.7605		0.0124
Van Laar	1.660	0.9185		0.0109
Wilson	1382	−235.6		0.0110
NRTL	−106.2	1226	0.2946	0.0110
Uniquac	−338.2	812.1		0.0112
Unifac				0.0589

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0240	0.2915	0.1946	0.6310	0.5714	0.7811	0.8378	0.8793
0.0267	0.3069	0.2257	0.6686	0.6119	0.8008	0.8809	0.9074
0.0355	0.3809	0.2628	0.6526	0.6557	0.7962	0.9042	0.9255
0.0924	0.5510	0.3086	0.6935	0.6983	0.8247	0.9398	0.9553
0.1230	0.5675	0.3705	0.7025	0.7804	0.8544	0.9551	0.9710
0.1601	0.5905	0.5163	0.7614	0.7980	0.8645	0.9684	0.9845

Table IX. Experimental Data and Fitted Parameters for the System *tert*-Butyl Alcohol (1)–*n*-Decane (2) at 70.1 °C

constants	A_{12}	A_{21}	α_{12}	mean dev in y
Margules	2.011	−0.7778		0.0200
Wilson	2089	−670.5		0.0073
NRTL	−667.9	2283	0.3008	0.0146
Uniquac	−554.1	1332		0.0142
Unifac				0.0374

x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
0.0041	0.4101	0.0817	0.8695	0.2125	0.9162	0.4093	0.9422
0.0150	0.6487	0.1121	0.8881	0.2437	0.9211	0.4509	0.9451
0.0488	0.8203	0.1314	0.8964	0.3067	0.9298	0.5024	0.9488
0.0588	0.8430	0.1600	0.9064	0.3325	0.9333	0.5997	0.9610
0.0666	0.8496	0.1857	0.9118	0.3763	0.9392	0.7054	0.9661
						0.9498	0.9946

also be used for the measurement of vapor–liquid equilibria of multicomponent systems: measurements are carried out here as described for binary systems.

The calibration must be carried out differently, however, since a two-dimensional plot of the percentage area vs. the composition is no longer possible. Instead, substance-specific correction factors are determined. The following relationship exists between mass fraction and integrated peak areas

$$g_i = \frac{A_i f_i}{\sum_j A_j f_j}$$

where g_i is the mass fraction of component i, A_i is the peak area of component i, and f_i is the substance-specific correction factor for component i. The calibration factors are largely concentration-independent. The use of a mean value is thus allowed, and such a procedure was chosen in the present case. Should a concentration dependence be observed, this must be taken into account. The vapor composition is calculated from the areas measured in the headspace analysis and the correction factors obtained from the above equation. The corrections of the liquid composition are carried out as described in ref *1*.

Results

The eight systems studied, together with the relevant mea-

Table X. Experimental Data and Fitted Parameters for the System Valeraldehyde (1)–Toluene (2)–1-Octene (3) at 44.7 °C

		Wilson		NRTL			Uniquac	
I	J	A_{IJ}	A_{JI}	A_{IJ}	A_{JI}	α_{IJ}	A_{IJ}	A_{JI}
1	2	141.5	−102.9	−188.8	272.4	0.302	−386.1	483.8
1	3	982.9	−276.0	−48.88	702.2	0.302	−266.6	492.4
2	3	377.6	−184.1	−271.0	590.8	0.299	138.3	−112.6
		0.0078[a]		0.0072[a]			0.0093[a]	

x_1	x_2	y_1	y_2	x_1	x_2	y_1	y_2	x_1	x_2	y_1	y_2	x_1	x_2	y_1	y_2
0.0732	0.0937	0.1915	0.1156	0.1966	0.2012	0.3295	0.2087	0.2984	0.3980	0.3878	0.3660	0.4980	0.2012	0.5802	0.1744
0.0991	0.2039	0.2182	0.2298	0.2015	0.2958	0.3211	0.2967	0.2815	0.5338	0.3703	0.4789	0.5018	0.2991	0.5783	0.2561
0.1072	0.3024	0.2091	0.3279	0.2047	0.3931	0.2981	0.3868	0.4059	0.0890	0.5504	0.0822	0.5014	0.3994	0.5705	0.3421
0.0908	0.4064	0.1649	0.4320	0.1992	0.4985	0.2839	0.4771	0.3968	0.2056	0.5124	0.1859	0.6001	0.1004	0.6739	0.0849
0.1029	0.4922	0.1800	0.5021	0.2358	0.5630	0.2723	0.5613	0.4000	0.2998	0.5015	0.2639	0.5999	0.1998	0.6611	0.1673
0.0987	0.6012	0.1536	0.5958	0.1950	0.6906	0.2595	0.6428	0.3995	0.4007	0.4902	0.3470	0.5994	0.3031	0.6531	0.2575
0.1020	0.6997	0.1483	0.6839	0.1979	0.7033	0.2611	0.6543	0.4009	0.5005	0.4745	0.4378	0.6990	0.1020	0.7418	0.0844
0.0961	0.8062	0.1290	0.7844	0.2949	0.1968	0.4325	0.1911	0.4785	0.0867	0.5923	0.0736	0.7033	0.1980	0.7369	0.1688
0.1965	0.0954	0.3567	0.1006	0.2976	0.2955	0.4131	0.2760	0.4997	0.1000	0.6086	0.0882	0.8037	0.0975	0.8203	0.0827

[a] Mean deviation.

Table XI. Pure-Component Properties

				Antoine constants		
component	v_i, mL/mol	r_i	q_i	A	B	C, mmHg
benzene	89.41	3.1878	2.4000	6.879 87	1196.76	219.161
toluene	106.85	3.9228	2.9680	6.950 87	1342.31	219.187
n-butyraldehyde	88.27	3.2479	2.8760	6.385 44	913.59	185.483
isobutyraldehyde	91.39	3.2471	2.8720	6.943 85	1162.60	222.0
valeraldehyde	106.41	3.9223	3.4160	7.019 20	1316.0	215.0
n-heptane	147.47	5.1742	4.3960	6.893 86	1264.37	216.64
n-octane	163.54	5.8486	4.9360	6.931 42	1358.80	209.855
n-decane	195.92	7.1974	6.0160	6.957 1	1503.57	194.738
tert-butyl alcohol	94.88	3.4528	3.1280	7.361 7	1180.93	180.476
1-octene	157.86	5.6185	4.7240	6.936 4	1355.78	213.022

Table XII. New Unifac Interaction Parameters

X	$a_{X/CHO}$, K	$a_{CHO/X}$, K
ACH	347.3	23.39
$ACCH_2$	586.8	106.0

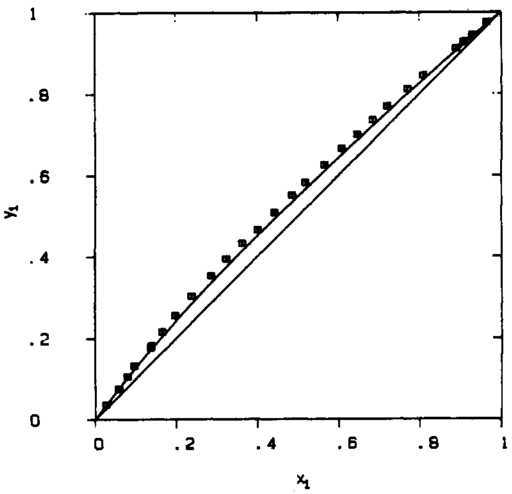

Figure 1. y–x diagram for the system valeraldehyde (1)–toluene (2) at 70.1 °C.

surement temperatures and the stationary phases used for the chromatographic separation, are listed in Table II. The experimental data and the fitted parameters for the Margules (*6*), van Laar (*7*), Wilson (*8*), NRTL (*9*), and Uniquac (*10*) equations are to be found in Tables III–X, which also contain the mean deviations of the mole fractions in the vapor phase calculated from the different models.

The function, which was used in fitting the parameters and the relations, which are valid for the parameter A_{ij} in Tables III–X, are described in the previous article (*1*). The parameters of the pure compounds, which are required for calculations using the different equations, are listed in Table XI. As expected, the alkane/*tert*-butyl alcohol systems show large deviations from Raoult's law. The aldehyde/aromatic systems show a much less accentuated real behavior. The measured VLE data of the aldehyde/aromatic systems were used to obtain new Unifac interaction parameters. Data reported by Naumann (*11*) were also taken into account in fitting the interaction parameters between the CHO and ACH/$ACCH_2$ groups. The new Unifac parameters are shown in Table XII. All other group interaction parameters used in the calculations were taken from ref *12* and *13*. VLE data for the alkane/*tert*-butyl alcohol systems were calculated by using the Unifac method and compared with the experimental values: the necessary parameters were also taken from ref *12* and *13*. The mean deviations of the mole fractions in the vapor phase as calculated by Unifac are given in Tables III–X for the various systems.

Figures 1–7 show the y–x diagrams of the four measured aldehyde/aromatic and the three measured alkane/*tert*-butyl alcohol systems. In the former the agreement between experimental and calculated values is extremly good. The deviations are however larger for the alkane/*tert*-butyl alcohol systems. Further investigations of systems containing *tert*-butyl alcohol taken from the Dortmund Data Bank have shown that these deviations are due to defects in the Unifac model. In the modified Unifac approach (*3*, *4*), which is still under development, the model is improved by introducing separate van der Waals values for primary, secondary, and tertiary alcohol groups.

As an example for the measurement of a multicomponent system we chose the ternary system 1-pentanol–toluene–1-octene, since this also allowed us to test the Unifac parameters

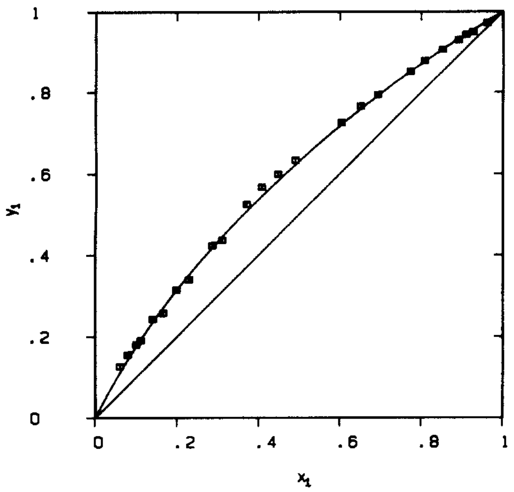

Figure 2. y–x diagram for the system isobutyraldehyde (1)–benzene (2) at 39.2 °C.

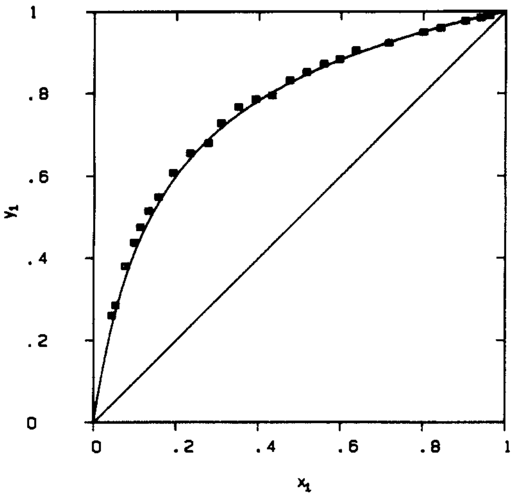

Figure 3. y–x diagram for the system isobutyraldehyde (1)–toluene (2) at 40.4 °C.

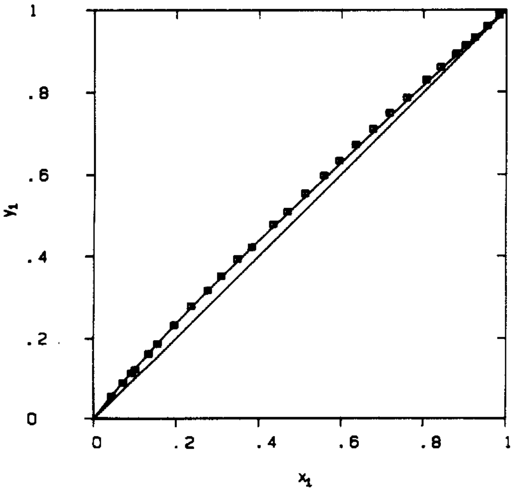

Figure 4. y–x diagram for the system n-butyraldehyde (1)–benzene (2) at 35.2 °C.

published in this and in the previous article on a ternary system. The calculation of this system using the group contribution method Unifac gave a mean absolute deviation in the vapor composition of 1.2 mol % with respect to the experimental data. There is thus also in this case good agreement between experimental and calculated values.

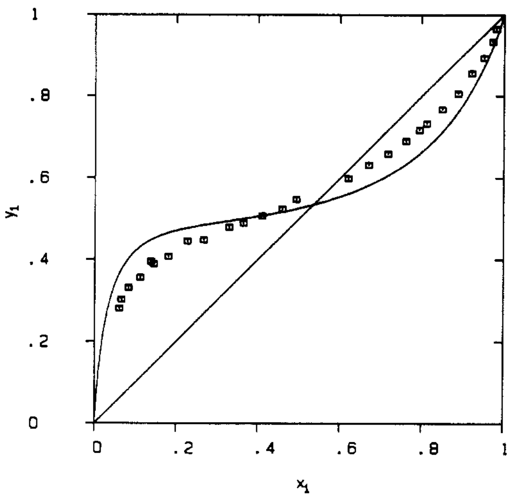

Figure 5. y–x diagram for the system n-heptane (1)–*tert*-butyl alcohol (2) at 60.1 °C.

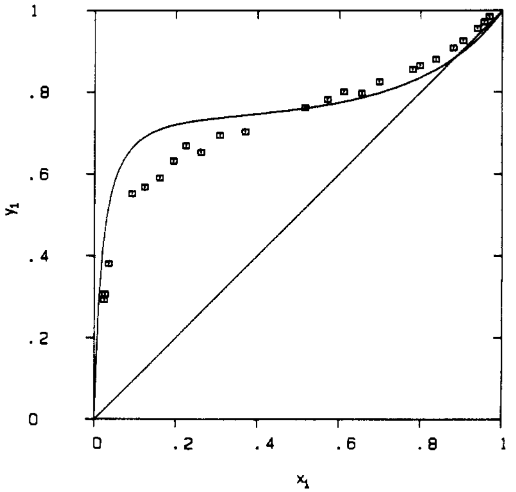

Figure 6. y–x diagram for the system n-octane (1)–*tert*-butyl alcohol (2) at 65.3 °C.

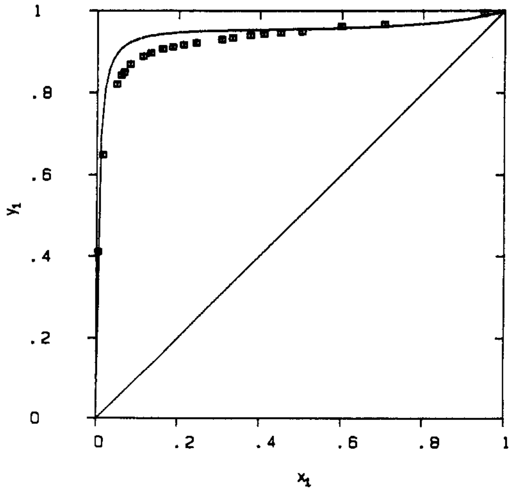

Figure 7. y–x diagram for the system *tert*-butyl alcohol (1)–n-decane (2) at 70.1 °C.

Conclusion

The results presented in this article support further the conclusion presented in ref 1 that gas chromatographic headspace analysis is a technique which allows the measurement of vapor–liquid equilibrium data of widely differing systems within a very short time. It is also clear that this technique can also be used without any problems for the measurement of systems containing more than two components.

Acknowledgment

We thank Professor U. Onken for his great interest in this work and G. Schlensog for his technical assistance.

Glossary

A, B, C	Antoine constants
A_i	peak area of component i
A_{ij}	parameters used in the Margules, van Laar, Wilson, NRTL, and Uniquac equations
a_{mn}	interaction parameter in the Unifac equation
f_i	substance-specific correction factor for component i
g_i	mass fraction of component i
q_i	relative van der Waals surface area of component i
r_i	relative van der Waals volume of component i
v_i	liquid molar volume of component i

Greek Letters

α_{12}	nonrandomness parameter in the NRTL equation

Registry No. Benzene, 71-43-2; toluene, 108-88-3; *n*-butyraldehyde, 123-72-8; isobutyraldehyde, 78-84-2; valeraldehyde, 110-62-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-decane, 124-18-5; *tert*-butyl alcohol, 75-65-0; 1-octene, 111-66-0.

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Viscosities of Solutions of Lithium Chloride in Water–Dimethyl Sulfoxide Mixtures at 25, 35, and 45 °C

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The viscosities and densities of a wide range of lithium chloride concentrations in water–dimethyl sulfoxide mixtures have been determined at 25, 35, and 45 °C. Jones–Dole *B* coefficients were calculated from the less concentrated solutions for 0.1, 0.3, 0.5, 0.7, and 0.9 mole fraction dimethyl sulfoxide solutions. Plots of Jones–Dole *B* coefficients vs. mole fraction show a positive deviation from linearity.

Introduction

Since early work by Jacob and co-workers (*1*) concerning the therapeutic promise of dimethyl sulfoxide, this compound has been the center of considerable controversy (*2*, *3*). However, it has been unequivocally shown that Me_2SO does enhance penetration through plant and animal membranes (*4*), and is particularly useful in enhancing percutaneous absorption (*5*, *6*). This property of Me_2SO is of special importance for enhancing the transdermal delivery rate of drugs (*7*).

Table I. Viscosity of Water-Me_2SO Mixtures at 25 °C

X_{Me_2SO}	η	X_{Me_2SO}	η
0.100	1.822	0.700	2.528
0.300	3.622	0.899	2.081
0.500	3.252		

With these applications in mind, an investigation of the transport properties of Me_2SO–water mixtures was considered of interest. This study reports on the viscosity measurements of a range of Me_2SO–water solutions with LiCl as an added electrolyte at 25, 35, and 45 °C. Viscosities of dilute electrolyte solutions can be analyzed in terms of the Jones–Dole equation (*8*).

$$\eta_{rel} = \eta/\eta_0 = 1 + AC^{1/2} + BC \qquad (1)$$

where η_{rel} is the relative viscosity, η is the measured viscosity, η_0 is the viscosity of the pure solvent, C is the molarity of the electrolyte, and A and B are the Jones–Dole coefficients.

The Jones–Dole A coefficient has been related to ion–ion interactions, and its value calculated theoretically (*9*). The B coefficient is related to ion–solvent interactions and has been used to make inferences concerning size, structure, and orientation of the solvated ion (*10*–*13*). Although many studies have considerable single solvent systems (*11*–*17*), fewer have used mixed solvent systems (*18*, *19*).

Experimental Section

Anhydrous LiCl (Fisher, Reagent) was dried at 125 °C for 2 h, cooled, and stored in a desiccator prior to sample preparation. Spectroscopic grade dimethyl sulfoxide was kept under nitrogen gas and used as received.

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