pressure. Particular attention has been given to the effect of water as an impurity in methanol, and evidence is given on how a small amount of water strongly influences LLE data for both binary and ternary systems.

The experimental data have been successfully correlated by NRTL and UNIQUAC models, and the interaction parameters were found to be temperature dependent.

Acknowledgment

We thank Mirna Cerovaz for the experimental work.

Glossary

rmsd	root-mean-square deviation defined in eq 1
x	liquid composition mole fraction
M	number of tie lines
T	temperature, K
S_{ij}	Solubility of component i in component j, mol %
δ	density, g/cm^3

Registry No. MeOH, 67-56-1; hexane, 110-54-3; cyclohexane, 110-82-7.

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Measurement of γ^∞ Using Gas–Liquid Chromatography. 3. Results for the Stationary Phases 10-Nonadecanone, *N*-Formylmorpholine, 1-Pentanol, *m*-Xylene, and Toluene

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In order to extend the range in which gas–liquid chromatography (GLC) can be used to measure activity coefficients at infinite dilution (γ^∞) to include more volatile stationary phases, we have constructed a modified gas chromatograph. Transport of solvent out of the column, which is the most significant error in the determination of γ^∞ by the GLC method, has been minimized by including thermostatic control accurate to 0.05 K, as complete as possible a saturation of the carrier gas with solvent, and a reduction of the pressure drop across the chromatographic separation column. The efficiency of the apparatus has been determined by comparison of our own measurements using the stationary phases 10-nonadecanone and *N*-formylmorpholine (NFM) with data from the literature. Results with the lighter solvents 1-pentanol, *m*-xylene, and toluene (at three temperatures in each case) are also reported. The vapor pressures of these solvents at measuring conditions lie between ca. 5 and ca. 80 mbar. The error in γ^∞ increases with increasing solvent volatility from 3% for nonvolatile stationary phases to ca. 10% for volatile solvents.

Introduction

Activity coefficients at infinite dilution are of interest for the development of liquid theories and are of great importance for the development and simulation of thermal separation processes. It is possible to estimate the variation of the activity coefficients across the complete concentration range with the help of a suitable thermodynamic model when only information on both boundary activity coefficients of a binary system is available: thus the vapor–liquid equilibrium (VLE) can be predicted.

The boundary activity coefficients γ^∞ (*1*), as well as VLE (*2*) and mixing enthalpy (*3*) data, serve as a database for the further development of liquid theories (in particular group contribution methods (*4*, *5*)). Activity coefficients at infinite dilution are of practical importance in the design of thermal separation plants for the production of very pure products. In particular the removal of the last traces of an impurity often requires a considerable amount of separation effort. Apart from ebulliometry, dilutor technique, and liquid–liquid chromatography, gas–liquid chromatography (GLC) is a rapid and exact method for the experimental determination of activity coefficients at infinite dilution. The calculation of these values by extrapolation from VLE measurements is subject to considerable errors. The GLC method normally involves the measurement of the retention of a sample of high vapor pressure at quasi-infinite dilution (solute) on a stationary phase (solvent) of very low vapor pressure.

In continuation of work carried out by Weidlich et al. (*6*, *7*) the present article deals with measurement of solutes on the technically more interesting, more volatile solvents using a gas chromatograph constructed by us.

The design of the gas chromatograph requires that the various elements be chosen on the basis of the tolerable degree of error. We were able to refer to an extensive literature dealing with gas chromatography in the measurement of thermodynamic quantities (*8*–*11*). Another apparatus also constructed specially for the requirements of the measurement of more volatile solvents has been described by Eckert et al. (*12*).

The number of systems whose activity coefficients at infinite dilution can be determined by using this modified technique is

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considerably increased, so that a broader database is available for the modified UNIFAC model or for fitting the parameters in g^E models. It is important to note that in addition boundary activity coefficients or separation factors for compounds of technical interest (e.g., for extractive rectification) can rapidly be obtained.

Theoretical Background

Gas chromatography can be regarded as a multistage separation process. The solute molecules present at infinite dilution interact with the molecules of the stationary phase as they pass through the column. The solute is held back more or less strongly, depending on the strength of the interactions.

The quantity used for comparisons between different experiments is the specific net retention volume v_g^0 corrected to 0 °C; this is given by the following equation relating the experimentally determined parameters:

$$v_g^0 = (t_R - t_A)\frac{273.15F}{m_L}\left[\frac{P_{fm} - P_W}{T_{fm}P_a}\right]\frac{3}{2}\left[\frac{(P_e/P_a)^2 - 1}{(P_e/P_a)^3 - 1}\right] \qquad (1)$$

t_R is the retention time of the solute, and t_A is the dead time required for an inert gas to pass through the column. F is the carrier gas volume flow at the soap bubble flowmeter at temperature T_{fm} and pressure P_{fm}. P_W is the saturation vapor pressure of water at T_{fm}, and P_e and P_a are the column inlet and outlet pressures, respectively.

The parameters mentioned previously are determined in the course of the gas-chromatographic measurements. m_L is the mass of solvent on the inert carrier material and can be determined from a subsequent analysis. In experiments using more volatile stationary phases it is impossible to avoid the loss of solvent due to a pressure drop across the column. In order to determine the actual mass of the stationary phase, an interpolation is carried out between the beginning and end of the series of measurements over the noted time at which a certain solute is injected.

The second expression in brackets in eq 1 converts the carrier gas flow rate via the ideal gas law, taking into account the water vapor pressure in the soap bubble flowmeter for the conditions at the column exit. The third expression in brackets (always less than unity) converts from column exit to mean column conditions, since the pressure drop across the column leads to an expansion of the gas and thus to an increase in the velocity of the carrier gas (volume flow). The activity coefficient at infinite dilution is then given by

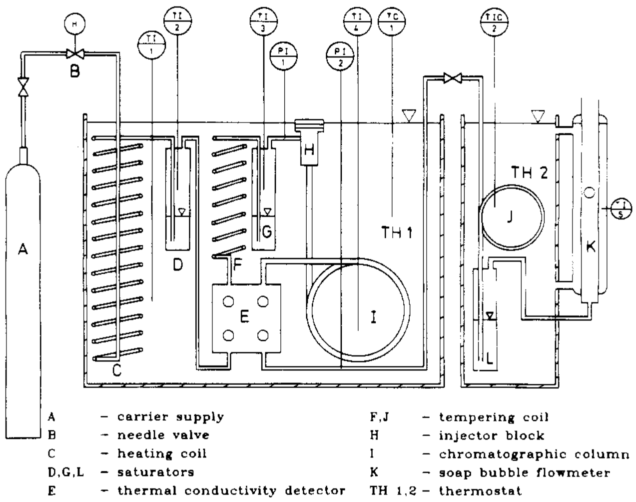
$$\gamma_i^\infty = \frac{273.15R}{v_g^0 \varphi_i^s P_i^s M_L} \qquad (2)$$

where R is the gas constant, M_L the molar mass of solvent, and P_i^s the saturation vapor pressure of the solute. P_i^s is calculated by use of Antoine constants taken from the Dortmund Data Bank (DDB). The saturation fugacity coefficient of the solvent φ_i^s is calculated according to the Soave equation of state (*13*); the necessary critical data and acentric factors are again taken from the DDB.

According to the temperature dependence of the activity coefficients at infinite dilution

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right)_{P,x} = \frac{\bar{h}_i^{E\infty}}{R} \qquad (3)$$

we should obtain a straight line when ln γ^∞ is plotted against $1/T$ for a temperature range that is not too large. In addition to a check of the measurements, this gives us the possibility of determining the partial molar excess enthalpy at infinite dilution $\bar{h}_i^{E\infty}$. A detailed derivation of the equation involved is to be found in ref *9*. We shall proceed to discuss briefly the preconditions and limits of the evaluation equation. Equation 1 assumes a linear section of the sorption isotherm which gives the ratio of the solute concentrations in the stationary and mobile phases. This can be satisfied by taking sufficiently small amounts of the solute sample. Conder and Young (*10*) suggest 0.1 μL, Laub and Pecsok (*11*) 0.1–0.5 μl as suitable volumes, depending on density and molecular weight. The retention should be caused only by interactions between solute and solvent. Adsorption on the solid support and at the gas–liquid interface is avoided by the use of an inert carrier and a sufficiently high coating of the carrier material with solvent. According to Conder and Young (*10*), there are substance combinations for which adsorption effects that can falsify the results still occur preferentially:



A – carrier supply
B – needle valve
C – heating coil
D,G,L – saturators
E – thermal conductivity detector
F,J – tempering coil
H – injector block
I – chromatographic column
K – soap bubble flowmeter
TH 1,2 – thermostat

Figure 1. Schematic of the experimental apparatus.

1. Adsorption at the gas–liquid interface occurs with increasing polarity of the solvent. This effect decreases again with increasing polarity of the solute.
2. Polar solutes on nonpolar stationary phases lead to adsorption at the gas–liquid interface, often accompanied by adsorption on the solid support.

The retention time t_R in eq 1 is determined for peak maxima. This retention is only identical with that of an average molecule when peaks are symmetrical. Peak asymmetries occur when small amounts of impurities in the injected solute cannot be separated on the column. In addition, nonlinear sorption isotherms, chemical reactions between solute and solvent, and adsorption phenomena can be the cause of tailing.

Solubility of the carrier gas in the stationary phase is not taken into account by eq 1; according to ref *9* this can be neglected at a column inlet pressure P_e of ca. 1.2 atm. The more volatile solvents have noticeable vapor pressures at the measurement temperatures, so that the mobile phase should in fact be considered as a ternary mixture of carrier gas, solute, and solvent.

Experimental Setup

Figure 1 schematically shows the homemade gas chromatograph. The carrier gas cylinder is fitted with a two-step reducing valve, through which a pressure of ca. 2 bar is applied. The carrier gas used, helium (>99.99%), has the advantage over nitrogen that it has a higher heat conductivity difference than the majority of the injected solutes. The inlet tube contains a Hoke bellows-type cutoff valve and two needle valves in series that are used to adjust the constant carrier gas flow. The second needle valve is a Hoke valve of the type Micro Mite. The carrier gas is warmed to the temperature set for the thermostat bath TH1 by means of the heating coil C (ca. 3 m long, stainless steel tubing, $^1/_8$-in. external diameter) before it enters the first solvent saturator D; the two saturation stages D and G consist of identical miniature packed columns. The top, which is a fitted carrier gas inlet tube to the gas distributor, at two temperature measurement positions (TI2, TI3) in the saturation vapor spaces, and a carrier gas exit, is screwed to a 130-mm-long cylindrical plug of 20-mm inner diameter.

Polypropylene rings are used for sealing the saturators off from the thermostat bath. The packing consists of small wire spirals made of stainless steel. The presaturated carrier gas flows through the reference channel of the thermal conductivity detector E and is then led to a further tempering coil F (ca. 2 m long) in order to correct for the heat of evaporation possibly removed in the first saturation step or for temperature variations caused by heat transfer from the heating wires in the detector. After passing through the second saturation stage, the carrier gas reaches the injection block H (Pye Unicam, low dead volume). The injection block is attached to a hollow Teflon cylinder and is also kept at the measurement temperature by TH1. The packed separation columns, consisting of $^1/_4$-in. stainless steel tubing (4.1-mm internal diameter) wound into coils, lie between injection block and detector.

The thermal conductivity detector E is a semidiffusion cell (Gow-Mac, Model 10-285, with 4 WX heating wires). The dead time of the detector is given as less than 1.5 s. The electrical supply to the detector is provided by a Pye Unicam catharometer, the sensitivity of which is adjusted via the bridge current and the base line via coarse and fine potentiometers. The retention times are measured by a Hewlett-Packard HP 3990A integrator, which is capable of noise filtering, an advantage when volatile solvents are used. The gas chromatograph can be subjected to excess pressure for the purpose of checking for leaks by means of a second bellows-type cutoff valve between the thermostat baths TH1 and TH2. TH1 is a 20-L circulating water bath (Lauda) with built-in heating and cooling coils and a regulator that guarantees a temperature constant to ±0.05 K. TH2 is a simple 5-L Haake circulation water bath with a contact thermometer (TIC2),which is used to keep the temperature in the double-wall soap bubble flowmeter K constant to within ±0.5 K. The conditioning of the gas to this temperature takes place in the ca. 3-m-long coiled tube J. A 25-cm^3 gas wash bottle serves to presaturate the gas with water. All elements in TH1 are fitted with Swagelok adapters made of stainless steel; only the separation column is fixed to the injector block by a simple rubber pinch seal. The connections in TH2 are in part Swagelok joints, but between the glass parts silicon tube connections are used. The tube connecting the wash bottle to the soap bubble flowmeter is isolated to avoid condensation and the formation of plugs of liquid that could lead to variations in the carrier gas volume flow and thus increase the electrical noise in the detector.

The column inlet pressure is measured by an expansion measurement strip (EMS) excess pressure gauge (Ohkura GPT 3000-E, pressure range 0–2 bar, error limit ±3 mbar). The column outlet pressure directly after the detector was measured by a capacitive absolute pressure gauge (Setra, Model 280E, measurement range 0–1724 mbar); the error limit is given as ±1.9 mbar at constant temperature and includes nonlinearity, hysteresis, and reproducibility. Both pressure converters are connected to 4 $^1/_2$ digit indicating instruments (Tilz Industriemesstechnik). The atmospheric pressure was read off using a precision mercury manometer (Wallace + Tiernan) accurate to ±1 mbar. Temperature measurements were carried out at two positions (TI1, TI4) in the thermostat bath TH1 in order to be able to observe temperature gradients. As in the case of TI2 and TI3, platinum resistance thermometers (PT-100) of class B with the option $^1/_3$ DIN are used. Their error is temperature-dependent, being 0.10 K at 0 °C and 0.26 K at 100 °C; the resolution of the indicator instruments used is 0.01 K. The noted errors of the thermometers are a consequence of the allowable tolerances of the resistances; they are thus of systematic origin and were corrected by a calibration.

The complete gas chromatograph in TH1 is connected via two Teflon cylinders at the injector and detector with a Plexiglass plate, above which the measuring instruments are situated. The complete apparatus can be raised and lowered by means of a lever system, the Plexiglass plate serving as the lid of the liquid bath.

Measurement Procedure

Some points of the measurement procedure will first be discussed, in particular the procedure for determining the mass of solvent on the carrier material since this incorporates the greatest error. The solid support used for all solvents was Chromosorb WAW DMCS 60-80 mesh. The coating of the predried Chromosorb was carried out with a suitable solubilizer in a rotary evaporator after removal of dust.

The liquid loading of the solid support in percent with the stationary phase

$$X = \frac{m_{\mathrm{stat}}}{m_{\mathrm{CS}}} \times 100\% \qquad (4)$$

(where m_{stat} is the mass of stationary phase and m_{CS} is the mass of Chromosorb) was adjusted to lie between 15 and 30%. The separation column is weighed several times during its preparation, the last weighing taking place before it is built into the gas chromatograph in order to be able to determine the solvent loss from a weighing carried out after a series of measurements. The completely filled apparatus is brought to the equilibrium temperature by keeping it (under carrier gas flow) for 1–2 h (depending on the temperature used) in the thermostated bath TH1. The time elapsing between the start of carrier gas flow and the actual measurement is used in the interpolation for the determination of the corresponding solvent mass. The solutes are injected using a 1- or 10-μL Hamilton syringe (sample volumes 0.1–0.2 μL); each solvent is generally injected twice. It was necessary to use a 10-μL syringe with the more volatile solvents in order to be able to distinguish between peaks and the electrical noise, which increases with increasing volatility.

The thermal conductivity detector must be used with bridge currents as low as possible in order to ensure a long lifetime for the heating wires at a sensitivity that is just sufficient. Because of the decreased quantity of heat discharged by the carrier gas saturated with the stationary phase, bridge currents of 100–120 mA are used for the more volatile solvents.

The thermostat bath TH2 is kept at a temperature ca. 10 K above that of TH1 to avoid condensation of solvent and the formation of liquid plugs, which lead to a considerable increase in the electrical noise. The decrease of the mass of stationary phase on the solid support is followed by repeated injection of a reference substance during the whole series of measurements.

Subsequent to a series of measurements the coated carrier material is removed from the column, mixed, and weighed into porcelain crucibles in samples of 0.4–1 g. The solvent is then evaporated from the solid support in a muffle furnace. Petsev et al. (*14*) determined that such a procedure is more exact than an extraction method, since inorganic components of the carrier are not extracted reproducibly. In a further article by Petsev (*15*) it is stated that the solvent is generally quantitatively removed from the carrier within 2 h at 400 °C. It must, however, be taken into account that pure uncoated Chromosorb also suffers a loss of weight under the stated conditions; this is due to the presence of strongly adsorbed water which is not re-

Table I. Origin and Purity of the Stationary Phases Used

Solids

solvent	supplier	purity, %	mp, °C
10-nonadecanone	EGA-Chemie	99	55–57

Liquids

solvent	supplier	GC anal. with FID, % by wt	water content,[a] % by wt	n^{25}_D(exptl)	n^{25}_D(ref *16*)
1-pentanol	Merck (for synthesis)	99.8	0.153	1.4080	1.408
N-formylmorpholine	Krupp-Koppers	99.8	0.172		
m-xylene	Merck (98.5% purity)	99.8	0.026	1.4947	1.495
toluene	Merck (p.a. 99.5%)	99.8	0.025	1.4940	1.494

[a] Karl Fischer method.

Table II. Operating Conditions for 10-Nonadecanone

temp, °C	69.80	80.12
column length, mm	1121	1121
inlet press., mbar	1159.7	1190.1
outlet press., mbar	1035.5	1021.3
flowmeter		
press., mbar	1007.4	995.2
temp, °C	32.46	32.58
flow rate, cm^3/min	54.45	58.67
amt of stationary phase, g	0.660 33	0.442 85
molar mass, g/mol	282.5	282.5

moved by predrying at 100 °C for 2 h.

Because of its volatility, this procedure could not be used for toluene: a nonnegligible amount of solvent evaporated during the emptying of the column and filling of the crucibles.

In these cases the mass of solvent on the column was determined by heating the latter in a stream of inert gas at a temperature much higher than the boiling point of the solvent. In order to be able to neglect the correction for weight loss of the uncoated carrier, the carrier material was dried overnight prior to coating at the temperature used for annealing the column. A control crucible experiment with the annealed carrier and a muffle furnace showed that the stationary phase had been quantitatively removed.

The correct functioning of the gas chromatograph was checked by means of comparative measurements on the stationary phases 10-nonadecanone ($C_{19}H_{38}O$) and *N*-formylmorpholine ($C_5H_9NO_2$) because these solvents had previously been used by Weidlich (*6*, *7*) with another apparatus and also because comparisons with a large amount of literature data are possible (*1*). In order of increasing volatility measurements were carried out at three temperatures for each of the solvents 1-pentanol, *m*-xylene, and toluene. The purities of the solvents used are given in Table I.

Results

Apart from γ^∞ and net retention volumes corrected to 0 °C, the following tables also contain the parameters valid during each measurement series.

Tables II and III contain the results for the stationary phase 10-nonadecanone, for which at 69.80 and 80.12 °C the largest deviation is shown by methanol. The combination of the polar solute methanol and the nonpolar solvent 10-nonadecanone is one of the problem combinations already mentioned, for which mixed reaction mechanisms occur. If the values for methanol, for which adsorption occurs at the phase boundary and on the carrier material, are excluded, the mean deviation between the present measurements and those of Weidlich (*6*) and Alessi (*17*, *18*) is ca. 3.5%. The mean deviation at the higher temperature is 2.35%. This lies within the range of the expected error and indicates that the present apparatus gives reliable results.

Tables IV and V contain the operating conditions and the data for NFM–hydrocarbon systems. Because of the volatility of *N*-formylmorpholine it is necessary to use presaturation with this solvent. In addition, Figures 2 and 3 permit a comparison with results reported by other authors at various temperatures. The results obtained clearly demonstrate the suitability of NFM as a solvent for extractive rectification in the separation of aliphatics and aromatics.

Table V shows good agreement between our own results and the data of Weidlich et al. (*7*) and van Aken and Broersen (*19*).

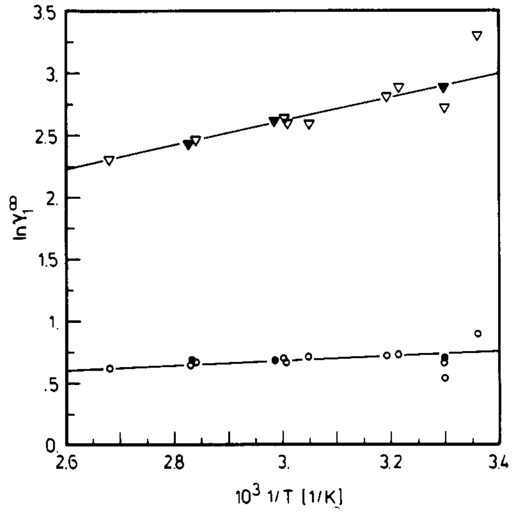


Figure 2. Activity coefficient at infinite dilution of benzene and cyclohexane in the selective solvent *N*-formylmorpholine. Benzene: ○, taken from ref *1*; ●, this work. Cyclohexane: ▽, taken from ref *1*; ▼, this work.

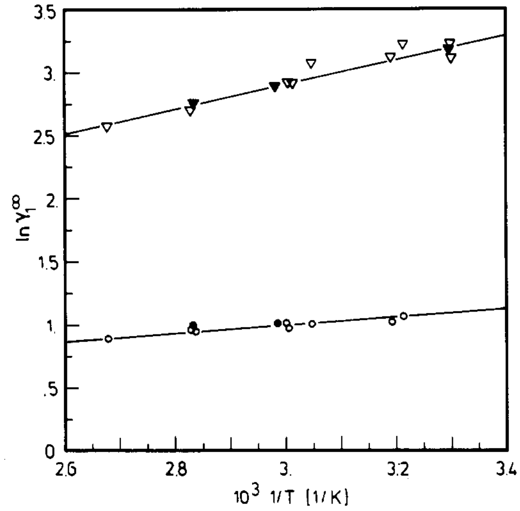


Figure 3. Activity coefficient at infinite dilution of toluene and methylcyclohexane in the selective solvent *N*-formylmorpholine. Toluene: ○, taken from ref *1*; ●, this work. Methylcyclohexane: ▽, taken from ref *1*, ▼, this work.

Table III. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for 10-Nonadecanone ($C_{19}H_{38}O$) in Comparison with Values from Ref *6*, *17*, and *18*

	69.80 °C		70.1–70.6 °C		rel devn, %		80.12 °C		80.5 °C		rel devn, %	
solute	v_g^0, cm^3/g	γ^∞	γ^∞ (ref *6*)	γ^∞ (ref *17, 18*)	ref *6*	ref *17, 18*	v_g^0, cm^3/g	γ^∞	γ^∞ (ref *6*)	γ^∞ (ref *17, 18*)	ref *6*	ref *17, 18*
n-pentane	32.15	0.957	0.983	1.00[a]	−2.64	−4.30	24.77	0.965	0.977	0.99	1.24	−2.54
n-hexane	79.74	1.003		1.05[a]		−4.48	59.65	0.993		1.02		−2.64
n-heptane	196.8	1.037	1.077	1.10[a]	−3.71	−5.73	140.5	1.026	1.067	1.04	−3.84	−1.35
n-octane	482.9	1.068	1.119	1.13[a]	−4.56	−5.49	325.5	1.068	1.112	1.09	−3.96	−2.02
1-hexene	76.53	0.891	0.931	0.92[a]	−4.33	−3.18	57.62	0.884	0.925	0.92	−4.49	−3.97
1-heptene	187.8	0.928		0.98[a]		−5.31	133.4	0.931		0.95		−2.00
1-octene	455.9	0.963	1.012	1.00[a]	−4.80	−3.66	306.3	0.976	1.006	0.99	−2.95	−1.38
ethyl acetate	90.67	1.149	1.197	1.17	−4.01	−1.79	65.71	1.132	1.173	1.14	−3.50	−0.70
toluene	454.7	0.663	0.686	0.65[a]	−3.35	2.00	315.4	0.663	0.694	0.66	−4.41	0.52
ethylbenzene	998.6	0.723		0.71[a]		1.87	658.1	0.731		0.72		1.58
benzene	176.8	0.637	0.661	0.64[a]	−3.69	−0.53	128.4	0.635	0.650	0.64	−2.29	−0.77
n-propyl acetate	218.6	1.109	1.160	1.09	−4.39	1.74	149.6	1.109	1.131	1.12	−1.95	−0.98
n-butyl acetate	539.5	1.051	1.106	1.04	−4.97	1.06	352.8	1.061	1.088	1.03	−2.48	3.01
methanol	21.22	3.115	2.616	2.94	19.07	5.95	16.17	2.815	2.238	2.65	25.78	6.23
ethanol	40.51	2.812	2.787	2.71	0.90	3.76	30.33	2.490	2.531	2.42	−1.62	2.89
1-propanol	106.1	2.366	2.433	2.25	−2.75	5.15	73.80	2.163	2.244	2.06	−3.61	5.00
mean abs dev, %					4.86	3.50					4.78	2.35

[a] Determined at 70.7 °C.

Table IV. Operating Conditions for *N*-Formylmorpholine

temp, °C	30.05	61.71	79.94
column, length, mm	1121	1510	1510
inlet press., mbar	1090.6	1261.2	1236.1
outlet press., mbar	1025.5	1028.5	1026.1
flowmeter			
press., mbar	999.7	999.6	100.7
temp., °C	32.23	31.15	35.16
flow rate, cm^3/min	22.85	48.29	38.65
amt of stationary phase, g			
start	0.609 59	1.009 0	1.035 7
end	0.607 99	0.975 57	0.990 31
molar mass, g/mol	115.1	115.1	115.1

Figures 2 and 3 also show a good agreement with values at other temperatures for the systems NFM–benzene (cyclohexane) and NFM–toluene (methylcyclohexane). In the case of the aliphatics (Figures 2 and 3) the result is optically less attractive, as no clear straight line can be drawn. However, our own results lie within the range of the literature data.

1-Pentanol has a considerably higher vapor pressure; the saturation vapor pressure is in the range 4–20 mbar for the temperatures used (see Table VI). The conditions used, the experimentally determined retention volumes, and the activity coefficients at infinite dilution are listed in Tables VII and VIII. As expected, alcohols show only a small deviation from ideal behavior; the deviations from Raoult's law are much larger for pure hydrocarbons and the remaining components in Table VII.

m-Xylene was studied at temperatures similar to those used for 1-pentanol; the saturation vapor pressures are given in Table IX and the conditions and experimental results in Tables X and XI. In contrast to pentanol, the largest deviation from ideal behavior is shown by the strongly polar alcohols with the stationary phase *m*-xylene.

In order to be able to detect an air peak clearly, a 10-μL syringe was used. The reduction of the measurement time and the use of a shorter column permit the solvent loss to be kept within limits.

The series of measurements carried out at 40 °C with the solvent toluene are associated with a further increase in vapor pressure (see Table XII). As for the stationary phase *m*-xylene, the largest deviations from Raoult's law are shown by the strongly polar alcohols (see Tables XIII and XIV).

In the case of the measurements at 20 °C it is possible to make a comparison with the literature data (*1*); the mean deviation between the two is 4.42%.

Discussion

Various literature references (*9*, *11*) point out that the measurement of solvent mass is the decisive error quantity in the determination of the specific net retention volume corrected to 0 °C. In his discussion of errors, Weidlich (*6*) has determined that the contributions of the operating parameters carrier gas flow rate, column inlet and outlet pressure, and temperature or pressure at the flowmeter to the error in v_g^0 are negligible in comparison with the contribution from the mass of stationary phase and the determination of the net retention time. The two procedures for the determination of the solvent mass, the crucible method and the method of heating in a current of inert gas, were subjected to an error propagation calculation. The result for the crucible experiment was that, in terms of to the error propagation, the contribution from the degree of liquid loading is the most important. The standard deviations for the two degrees of coating were determined from the four to six available crucibles per mass determination experiment, while the weighing error is taken as the standard deviation for the weight m_{ein}. In the heating method the solvent mass is the difference of two weight determinations, so that the standard deviation is constant.

In the case of the nonvolatile solvent 10-nonadecanone the error in the determination of the activity coefficient at infinite dilution is calculated from a consideration of all sources of error to be 3%. In all other series of measurements there is a weight loss of solvent, which is corrected for by a linear interpolation. The standard deviation in the boundary activity coefficient of a reference substance that is added repeatedly during the whole time of measurement, the γ^∞ of which was corrected according to the stated procedure, is taken as an approximate value for the error of the interpolation. The resulting errors are the sums of the approximate values and the above 3%: for *N*-formylmorpholine, 4.50–6.35%; for 1-pentanol, 4.50–5.3%; for *m*-xylene, 3.11–4.7%; and for toluene, 3.62–6.43%. Because of the uncertainty of this method for estimating errors, error quantities determined by Eckert et al. for γ^∞ measurements on volatile solvents using the GLC method will be quoted: in ref *12* they state their measurements to be correct within 2–5%. The discussion of errors is differentiated in a later publication by this group (*20*): the error of 5% applies to the reproducibility and consistency within their own measurements, while they estimate the absolute error for boundary activity coefficients < 100 to be 15%. However, the solvents used by them are in part more volatile than those used

Table V. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for *N*-Formylmorpholine ($C_5H_9NO_2$) in Comparison with Values from Ref *1* and *7*

solute	30.05 °C		30.0 °C	rel devn, %	61.71 °C		59.5 °C	60.0 °C	rel devn, %		79.94 °C		79.3 °C	80.0 °C	rel devn, %	
	v_g^0, cm^3/g	γ^∞	γ^∞(ref *1*)	ref *1*	v_g^0, cm^3/g	γ^∞	γ^∞(ref *7*)	γ^∞(ref *1*)	ref *7*	ref *1*	v_g^0, cm^3/g	γ^∞	γ^∞(ref *7*)	γ^∞(ref *1*)	ref *7*	ref *1*
n-pentane	9.65	25.66	26.0	−1.31			19.29	19.10					16.36	15.5		
n-hexane	23.10	34.64	35.2	−1.59	10.24	24.67	24.61	25.4	0.24	−2.87	6.96	20.99	20.62	20.5	1.79	2.39
n-heptane	54.32	46.68	47.5	−1.73	20.89	32.06	31.36	33.1	2.23	−3.14	13.37	26.62	26.13	26.3	1.88	1.22
n-octane	126.5	63.35	63.4	−0.08	42.16	41.78	40.67	42.2	2.73	−1.00	25.69	33.43	33.65	33.1	−0.65	1.00
isooctane	45.44	52.42			17.87	36.93	36.02		2.53		11.99	29.87	30.69		−2.67	
n-decane			114.0		171.1	69.78	65.81	69.5	6.03	0.40	92.38	52.87	53.25	49.9	−0.71	5.95
methylcyclopentane	46.23	18.99			19.15	14.41	14.21		1.41		12.71	12.51	12.49		0.16	
cyclohexane	68.27	17.90	17.9	0.00	26.56	13.77	13.52	13.9	1.85	−0.94	17.61	11.68	11.73	11.5	−0.43	1.57
methylcyclohexane	104.8	24.11	24.7	−2.39	37.78	18.36	18.51	18.6	−0.81	−1.29	24.19	15.47	15.57	15.0	−0.64	3.13
ethylcyclohexane	265.6	33.25	33.0	0.76	86.46	23.19	23.26	23.8	−0.30	−2.56	51.21	19.32	19.14	19.1	0.94	1.15
o-xylene					976.3	3.451	3.354		2.89		480.9	3.269	3.234		1.08	
p-xylene					708.4	3.784	3.838		−1.41		344.4	3.705	3.714		−0.24	
m-xylene					753.2	3.702	3.808		−2.78		361.9	3.647	3.675		−0.76	
ethylbenzene					687.3	3.619	3.602	3.66	0.47	−1.12	336.5	3.535	3.587	3.42	−1.45	3.36
toluene					366.8	2.738	2.652	2.75	3.24	−0.44	191.4	2.700	2.584	2.62	4.49	3.05
benzene	614.9	2.025	1.96	3.32	182.2	1.988	1.962	1.99	1.33	−0.10	101.0	1.993	1.943	1.93	2.57	3.26
trans-1,4-dimethylcyclohexane					54.15	23.51	24.32		−3.33		31.64	20.75	20.67		0.39	
cis-1,4-dimethylcyclohexane					71.46	21.35	22.68		−5.86		40.92	18.89	18.44		2.44	
trans-1,2-dimethylcyclohexane					66.73	21.74	23.08		−5.81		38.84	19.11	18.71		2.13	
cis-1,2-dimethylcyclohexane					93.09	19.66	20.59		−4.52		52.63	17.37	17.56		−1.08	
mean abs devn, %				1.40					2.62	1.39					1.39	2.61

Table VI. Vapor Pressure of 1-Pentanol

T, °C	P_i^s, mbar
30.28	4.89
40.00	9.81
50.27	19.20

Table VII. Operating Conditions for 1-Pentanol

temp, °C	30.28	40.00	50.27
column length, mm	1121	1121	1121
inlet press., mbar	1116.9	1179.4	1149.2
outlet press., mbar	1033.8	1034.9	1032.7
flowmeter			
press., mbar	1008.8	1009.3	1005.4
temp, °C	33.8	33.13	33.03
flow rate, cm^3/min	40.04	44.23	43.20
amt of stationary phase, g			
start	0.42540	0.73127	0.72003
end	0.39020	0.65077	0.63483
mass loss, %	8.27	11.01	11.83
molar mass, g/mol	88.15	88.15	88.15

Table VIII. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for 1-Pentanol

	30.28 °C		40.00 °C		50.27 °C	
solute	v_g^0, cm^3/g	γ^∞	v_g^0, cm^3/g	γ^∞	v_g^0, cm^3/g	γ^∞
n-pentane	83.9	3.825	60.73	3.816	45.92	3.675
n-hexane	252.1	4.107	172.1	4.095	122.3	3.959
n-heptane	707.7	4.629	444.8	4.726	307.5	4.432
n-octane			1583	3.937		
isooctane	645.8	4.766	412.2	4.869	287.7	4.611
1-hexene	243.3	3.487	162.3	3.599	117.6	3.448
1-heptene	680.6	3.946	436.6	3.992	299.9	3.812
methanol	1013.5	1.153	654.0	1.120	410.2	1.131
ethanol			1295	1.117	777.9	1.118
ethyl acetate	641.9	2.495	447.4	2.323	317.2	2.150
n-propyl acetate	1419.	3.169	999.8	2.776	788.1	2.198
diethyl ether	183.6	1.667	132.0	1.659	94.3	1.674
acetone	290.8	2.336	215.3	2.153	160.2	1.993
methyl ethyl ketone	793.8	2.120	548.1	2.009	392.3	1.854
cyclohexane	483.3	3.271	320.4	3.301	224.2	3.186
methylcyclopentane	338.5	3.355	235.3	3.282	164.9	3.214
butanal	479.9	2.867	346.5	2.618	251.2	2.416
benzene	620.6	2.595	411.2	2.594	285.6	2.500
toluene	1705	3.058	1128	2.910	729.5	2.862
dichloromethane	201.9	1.819	147.0	1.757	102.8	1.779
1,1,2-trichlorotrifluoroethane	120.7	3.992	89.22	3.806	64.77	3.728

Table IX. Vapor Pressure of *m*-Xylene

T, °C	P_i^s, mbar
30.42	15.08
40.31	25.65
50.44	42.41

Table X. Operating Conditions for *m*-Xylene

temp, °C	30.42	40.31	50.44
column length, mm	706	706	706
inlet press., mbar	1111.9	1117.5	1128.0
outlet press., mbar	1034.4	1023.9	1016.0
flowmeter			
press., mbar	1004.5	995.7	986.5
temp, °C	36.53	44.45	51.83
flow rate, cm^3/min	49.96	48.59	54.76
amt of stationary phase, g			
start	0.80797	0.81596	0.69245
end	0.75517	0.71396	0.57595
mass loss, %	6.53	12.50	16.82
molar mass, g/mol	106.2	106.2	106.2

in the present work, and their solvent mass determination is carried out by adding (from a syringe) a substance of known γ^∞, so that it is possible to calculate back and obtain the mass.

Table XI. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for *m*-Xylene

	30.42 °C		40.31 °C		50.44 °C	
solute	v_g^0, cm^3/g	γ^∞	v_g^0, cm^3/g	γ^∞	v_g^0, cm^3/g	γ^∞
n-pentane	173.3	1.530	122.3	1.558	93.67	1.489
n-hexane	570.7	1.497	370.2	1.562	266.4	1.500
1-hexene			355.4	1.348	268.8	1.246
acetone	266.7	2.102	177.6	2.143	131.3	2.008
methyl ethyl ketone			559.3	1.613	382.4	1.569
methanol	50.49	19.08	35.36	16.96	28.24	13.54
ethanol	133.4	15.03	89.04	13.27	66.38	10.78
1-propanol			288.6	10.55	207.0	8.380
2-propanol	238.8	11.29	156.6	9.929	113.5	8.101
diethyl ether	230.5	1.097	154.5	1.164	114.5	1.139
ethyl acetate			617.5	1.379	424.3	1.325
cyclohexane					452.2	1.303
butanal					375.5	1.334
dichloromethane	379.1	0.800	253.4	0.837	180.3	0.837
1,1,2-trichlorotrifluoroethane	233.3	1.706	160.8	1.735	120.7	1.652

Table XII. Vapor Pressure of Toluene

T, °C	P_i^s, mbar
20.0	29.09
30.01	48.89
40.0	78.86

Table XIII. Operating Conditions for Toluene

temp, °C	20.00	30.01	40.00
column length, mm	706	706	706
inlet press., mbar	1099.7	1107.5	1100.1
outlet press., mbar	1032.6	1033.2	1021.1
flowmeter			
press., mbar	1002.5	1002.0	994.1
temp, °C	33.67	38.37	48.90
flow rate, cm^3/min	43.20	44.64	41.02
amt of stationary phase, g			
start	0.62970	0.54805	0.98200
end	0.57210	0.45545	0.74160
mass loss, %	9.15	16.90	24.48
molar mass, g/mol	92.14	92.14	92.14

Table XIV. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for Toluene

	20.00 °C		30.01 °C		40.00 °C	
solute	v_g^0, cm^3/g	γ^∞	v_g^0, cm^3/g	γ^∞	v_g^0, cm^3/g	γ^∞
methanol	88.87	21.42	61.32	18.49	40.41	17.35
ethanol	243.7	17.34	155.8	15.17	92.88	14.90
2-propanol	437.7	13.24	282.0	11.28	173.4	10.51
dichloromethane	633.7	0.831	423.2	0.839	246.3	1.002
n-pentane	240.9	1.853	174.4	1.778	113.9	1.949
n-hexane	822.2	1.873	564.9	1.774	349.6	1.928
1-hexene	866.4	1.439	575.0	1.427	361.0	1.549
diethyl ether	386.0	1.115	264.9	1.116	169.1	1.238
acetone	511.8	1.967	341.2	1.926	213.0	2.083

Conclusion

The apparatus constructed by us gives reliable results and makes it possible by means of exact thermostating, carrier gas saturation, and the use of short columns to measure γ^∞ for many volatile solvents. The error in the γ^∞ value increases with increasing volatility of the solvent. If only the separation factor of the components to be separated is required, the main sources of error in the determination of γ^∞ are eliminated. The apparatus discussed here is thus ideally suited for the direct determination of the separation factors, i.e., the selective influence of extracting solvents.

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

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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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