J. Chem. Eng. Data 1987, 32, 138–142

Measurement of γ^∞ Using Gas–Liquid Chromatography. 1. Results for the Stationary Phases *n*-Octacosane, 1-Docosanol, 10-Nonadecanone, and 1-Eicosene

Ulrich Weidlich[†] **and Jürgen Gmehling***

Universität Dortmund, Lehrstuhl für Technische Chemie B, 4600 Dortmund 50, FRG

For fitting the required group interaction parameters in the modified UNIFAC method h^E and γ^∞ data as well as VLE data are used. To complete the available data base, activity coefficients at infinite dilution of various classes of substances at three different temperatures on *n*-octacosane, 1-docosanol, 10-nonadecanone, and 1-eicosene were measured by using gas–liquid chromatography. The quantity which was most difficult to obtain from the actual measurement parameters in the determination of activity coefficients at infinite dilution (or the specific retention volume) is the mass of the stationary phase in the column. This was determined thermogravimetrically. From the law of propagation of error, a standard deviation of 3% for the measured activity coefficient at infinite dilution was calculated.

Introduction

The measurement of activity coefficients at infinite dilution γ^∞ using gas chromatography provides a simple but very exact alternative to conventional methods for determining vapor–liquid equilibrium data. The conventional dynamic and static methods in particular require a relatively large experimental effort with respect to both purification of the substances and to the actual measurement of the vapor–liquid equilibrium. This means that such measurements are extremely expensive when carried out in industrial laboratories. In contrast, reliable γ^∞ measurements can be carried out rapidly and at much less cost. The experimental setup is simple and the amount of substance required is small. Further advantages are present, due to the fact that gas–liquid chromatography retains its character as a separation technique when used in physicochemical applications. When the separation column is of an appropriate type, several substances to be investigated can be subjected to measurement in one single experiment. However, even more important is the fact that an extreme purification of the substances is not required, since impurities are removed during the passage through the column.

The basic idea of γ^∞ measurements is to use the information on the boundary activity coefficients to predict the variation of the activity coefficients across the whole concentration range, and thus to predict the complete vapor–liquid equilibrium with the help of a suitable thermodynamic model. In addition, an exact description of the real behavior of a mixture at extreme dilution is a component of great technical importance. In the case of positive deviation from Raoult's law the separation of such mixtures often requires a very large number of theoretical plates in a rectification column. Examples are purification of exhaust gases and of waste water and the preparation of substances of very high purity.

The two most important gas-chromatographic techniques for the determination of boundary activity coefficients are the retention time method (which is used in the present work) and the method of stripping of a mixture. In addition there exist ebulliometric methods, in which the activity coefficient at infinite dilution is determined from the temperature or pressure change occurring when small amounts of a substance are added to a solvent.

The retention time method is described, together with a literature survey, by Laub and Pescok (*1*) among others. Leroi et al. (*2*) describe the method of stripping a mixture of substances. A description of the different techniques for determining activity coefficients at infinite dilution can be found in Tiegs et al. (*3*). This data compilation also reports the data on activity coefficients obtained by the different techniques (approximately 16 000 γ^∞-values).

Theoretical Background

The activity coefficient at infinite dilution γ^∞ cannot be measured directly, but must be calculated from the retention time (retention time method) and other measured parameters. The reader is referred to the book by Laub and Pescok (*1*) for the derivation of the corresponding equations. The characteristic gas-chromatographic quantity, which can be found in the literature for many substances and various stationary phases, is the specific retention volumes V_g^0 (corrected to 0 °C).

$$V_g^0 = (t_R - t_A)\,\frac{273.15F}{T_{fm}m_L}\left[\frac{p_{fm} - p_w}{p_{fm}}\right]\frac{3}{2}\left[\frac{(p_E/p_A)^2 - 1}{(p_E/p_A)^3 - 1}\right] \qquad (1)$$

where V_g^0 is the specific retention volume (corrected to 0 °C), t_R the retention time, t_A the dead time (retention time of an inert gas), F the gas flow, T_{fm} the temperature at the flow meter in K, p_{fm} the pressure at the flow meter, p_E the pressure at the column entrance, p_A the pressure at the column exit, m_L the mass of stationary phase, and p_w the vapor pressure of water at T_{fm}.

The activity coefficient at infinite dilution can be determined from the specific retention volume V_g^0 by using the following equation:

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

Here V_g^0 is the specific retention volume (corrected to 0 °C), γ^∞ the activity coefficient at infinite dilution, M_L the molecular weight of the stationary phase, P_i^s the vapor pressure of component i, R the gas constant, and φ_i^s the fugacity coefficient of the component i in the saturated state. The fugacity coefficients in the saturated state φ_i^s were obtained in this work from the Soave equation (*4*) as modified by Graboski and Daubert (*5*).

Apparatus and Measurements

The measurements were carried out with a Perkin-Elmer gas chromatograph F45. The retention and dead times were

---

[†] ZBFE-Zentrale/Verfahrenstechnik, Hüls AG, D-4370 Marl, FRG.

0021-9568/87/1732-0138$01.50/0

measured by using a Hewlett Packard integrator HP 3390A connected to a thermal conductivity detector. The flow rate of the carrier gas was determined by using a soap-bubble flow meter. To ensure saturation of the carrier gas with water (this is taken into account in eq 1 for the calculation of the specific retention volume) it was passed through a wash bottle filled with water before entering the flow meter. The temperature at the flow meter was measured by a resistance or a mercury thermometer. To avoid large temperature variations at the flow meter due to changes in room temperatures, the flow meter and thermometer were tightly enclosed in a glass tube.

A piezo-resistive pressure gauge with an amplifier, a normalized current exit signal, and a digital indicator (WIKA) was used to measure the pressure at the entrance to the column. This pressure gauge permits measurements over the range 0–2.5 bar (accuracy class: 0.1). The pressure at the column exit, which is identical with that at the flow meter, was measured by Wallace & Tiernan mercury manometer.

The oven temperature was determined by using an iron–constantan thermocouple, values being read off from a FLUKE digital thermometer Model 2170A. Helium was used as the carrier gas, and the columns were 2 m long with an external diameter of $^1/_4$ in. The solid support for the stationary phases *n*-octacosane, 1-docosanol, 10-nonadecanone, and 1-eicosene was Chromosorb P AW D MCS (60–80 mesh); the liquid loading was approximately 25%. The substances (ca. 0.2 μL in each case) were injected via the injector block by using a 1-μL syringe. The determination of the mass of the stationary phase was carried out gravimetrically. Two methods were available: thermoanalysis and the direct evaporation of the stationary phase in an oven. The thermoanalysis is carried out as follows: an exactly known amount of solid support coated with the stationary phase is heated on a balance under nitrogen. The stationary phase evaporates, and the solid support remains: the exact liquid loading can be calculated from the weight loss, and thus the mass of stationary phase in the column can be obtained.

The method permits the determination of substances which are oxygen-sensitive, since a nitrogen atmosphere is used. In addition, mixtures whose components evaporate at different temperatures can be analyzed, since the weight loss can be followed continuously by using a pen recorder. In this work we used only pure substances, which are not oxygen-sensitive, as stationary phases: thus we used the equally exact method of direct mass measurement by heating the substances in an oven. The substances were introduced into crucibles specially constructed for gravimetric analysis, the crucibles were weighed, heated in an oven to a temperature sufficient to ensure complete evaporation of the stationary phase (500–800 °C), and weighed again after being allowed to cool in a desiccator. The mass measurements were carried out several times before and after each series of measurements, to check whether a weight loss had occurred during the measurements.

The measurement temperature was chosen so that no noticeable weight loss of the stationary phase by evaporation was possible. This was checked by determining the specific retention volume of a particular substance at different times. In the case of the measurements described here, no weight loss occurred over the chosen temperature range.

Results

The boundary activity coefficients of various types of substances were determined at three different temperatures using four different stationary phases. The substances were partially chosen according to the temperature range available for the particular stationary phase: thus several high-boiling substances could not be studied at low temperatures, since the expected retention times would have been too long. It should be noted that long retention times in combination with relatively broad peaks can lead to errors. The stationary phases used were *n*-octacosane ($C_{28}H_{58}$), 1-docosanol ($C_{22}H_{46}O$), 10-nonadecanone ($C_{19}H_{38}O$), and 1-eicosene ($C_{20}H_{40}$).

Table I. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for the Stationary Phase *n*-Octacosane ($C_{28}H_{58}$)

	80.2 °C		100.3 °C		120.2 °C	
	V_g^0	γ^∞	V_g^0	γ^∞	V_g^0	γ^∞
n-pentane	24.4	0.693	15.7	0.688	10.7	0.694
n-heptane	138.4	0.744	74.8	0.751	44.1	0.757
n-octane	320.5	0.774	156.2	0.798	86.8	0.794
isooctane	128.0	0.809	71.5	0.806	42.9	0.812
n-decane	1689.0	0.833	693.3	0.864	334.8	0.858
cyclohexane	104.2	0.571	60.6	0.571	37.7	0.574
methylcyclohexane	181.6	0.596	100.3	0.596	59.8	0.614
1-hexene	50.5	0.719	30.6	0.715	19.5	0.724
1-octene	272.0	0.785	138.8	0.785	77.6	0.787
methanol	4.5	7.230	3.59	4.788	2.90	3.377
ethanol	8.85	6.085	6.09	4.349	4.48	3.208
1-propanol	22.2	5.131	14.2	3.665	9.23	2.958
2-propanol	13.5	4.737	8.96	3.288	6.17	2.668
1-butanol	56.6	4.692	32.8	3.404	20.4	2.598
tert-butanol	19.5	3.352	12.8	2.482	8.67	1.961
1-pentanol	131.4	4.382	70.6	3.295	42.2	2.538
3-methyl-1-butanol	106.9	4.209	57.0	3.202	34.6	2.445
1-hexanol	304.5	4.212	151.7	3.226	85.3	2.491
1-heptanol	735.9	4.277	327.3	3.213	172.9	2.424
1-octanol			683.2	3.192	338.4	2.434
methyl acetate	17.6	1.657	11.5	1.476	7.74	1.382
ethyl acetate	35.7	1.498	21.9	1.368	13.9	1.311
propyl acetate	84.0	1.410	46.9	1.300	28.3	1.215
butyl acetate	195.9	1.364	101.5	1.276	58.1	1.197
ethyl propionate	82.9	1.301	46.1	1.229	28.2	1.156
ethyl butyrate	180.9	1.192	93.9	1.162	55.0	1.096
vinyl acetate	28.5	1.620	17.8	1.459	11.5	1.370
acetone	12.6	2.272	8.59	1.965	6.05	1.767
2-butanone	32.9	1.747	20.6	1.548	13.2	1.448
2-pentanone	73.2	1.612	41.9	1.482	25.7	1.392
3-pentanone	80.2	1.461	45.6	1.353	28.0	1.267
4-methyl-2-pentanone	117.4	1.558	65.2	1.436	39.8	1.328
4-heptanone	357.3	1.486	173.5	1.412	97.1	1.293
2-octanone			407.3	1.681	204.5	1.539
n-butanal	33.4	1.513	21.0	1.404	13.8	1.349
2-methylpropanal	25.2	1.437	16.4	1.298	10.9	1.233
n-pentanal	82.2	1.471	47.4	1.342	29.0	1.261
crotonaldehyde	50.7	2.297	30.5	2.001	19.5	1.782
furfurol	203.7	5.831	105.9	4.687	63.3	3.623
benzene	89.0	0.647	52.3	0.629	32.6	0.621
toluene	221.9	0.673	118.4	0.666	69.7	0.648
o-xylene	635.9	0.713	308.3	0.707	165.8	0.695
m-xylene	542.3	0.703	265.3	0.699	142.9	0.695
p-xylene	538.4	0.684	264.0	0.683	141.7	0.685
chlorobenzene	394.4	0.751	200.5	0.736	113.2	0.710
styrene			293.0	0.768	158.4	0.749
aniline					191.2	2.246
1-bromopropane	60.1	0.737	36.7	0.698	23.6	0.678
thiophene	89.8	0.732	53.0	0.693	34.1	0.652
tetrachloromethane	90.6	0.584	53.1	0.585	33.9	0.576
dimethyl sulfoxide	195.0	13.55	101.9	10.58	63.7	7.83
dibutyl ether			237.1	0.840	126.3	0.827

The results are collected in Tables I–IV. These contain not only the activity coefficients at infinite dilution but also the specific retention volumes corrected to 0 °C. This is desirable, since the retention volumes form the actual experimental parameters: the boundary activity coefficients are obtained from them by using eq (2). Comparison with the results of other groups are given in Tables V and VI. Figure 1 shows the results for the solutes ethanol, *n*-octane, and benzene for different temperatures on the stationary phase 10-nonadecanone.

Table II. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for the Stationary Phase 1-Docosanol ($C_{22}H_{46}O$)

	80.4 °C		90.1 °C		99.9 °C	
	V_g^0	γ^∞	V_g^0	γ^∞	V_g^0	γ^∞
n-pentane	18.3	1.107	14.9	1.089	12.4	1.065
n-heptane	98.9	1.250	74.0	1.233	55.8	1.230
n-octane	226.9	1.311	161.1	1.309	117.5	1.298
isooctane	90.7	1.372	68.5	1.356	52.8	1.335
cyclohexane	81.0	0.883	61.6	0.885	48.1	0.878
methylcyclohexane	136.7	0.951	102.8	0.940	78.2	0.933
1-hexene	40.0	1.093	31.7	1.069	24.8	1.075
1-octene	207.5	1.234	150.3	1.218	111.3	1.198
methanol	27.4	1.424	19.2	1.490	14.4	1.464
ethanol	47.7	1.354	33.8	1.333	24.5	1.327
1-propanol	110.4	1.236	75.1	1.225	52.1	1.220
2-propanol	65.8	1.170	45.6	1.164	32.6	1.155
1-butanol	259.9	1.224	170.4	1.209	115.6	1.185
tert-butanol	80.0	0.981	55.9	0.976	39.7	0.977
3-methyl-1-butanol	463.3	1.162	298.4	1.148	195.6	1.146
methyl acetate	27.5	1.273	22.0	1.215	18.4	1.131
ethyl acetate	54.7	1.175	42.8	1.125	34.3	1.069
propyl acetate	123.1	1.154	90.8	1.123	70.4	1.060
butyl acetate	282.6	1.134	202.9	1.100	150.3	1.056
ethyl propionate	116.7	1.110	86.9	1.080	66.6	1.040
ethyl butyrate	244.1	1.060	175.3	1.051	130.7	1.021
vinyl acetate	36.8	1.506	29.8	1.394	24.2	1.306
acetone	25.7	1.337	20.5	1.289	17.0	1.214
2-butanone	58.4	1.181	45.8	1.127	36.9	1.057
acetone	120.2	1.178	90.8	1.132	70.8	1.073
3-pentanone	125.0	1.125	93.2	1.095	72.5	1.040
4-methyl-2-pentanone	184.4	1.190	135.7	1.157	104.1	1.101
4-heptanone	520.5	1.223	362.4	1.194	260.5	1.153
n-pentanal	138.4	1.048	101.8	1.035	76.6	1.015
crotonaldehyde	96.3	1.452	73.9	1.371	57.6	1.295
furfurol	398.0	3.574	295.3	3.124	210.0	2.904
benzene	85.1	0.812	65.2	0.803	51.3	0.785
toluene	207.0	0.866	151.0	0.863	115.5	0.834
o-xylene	598.4	0.909	415.8	0.907	301.1	0.886
m-xylene	498.7	0.916	350.8	0.910	255.2	0.890
p-xylene	490.3	0.901	347.3	0.891	252.0	0.876
chlorobenzene	396.8	0.896	286.2	0.878	209.4	0.863
1-bromopropane	59.7	0.892	47.4	0.855	37.4	0.838
tetrachloromethane	79.6	0.799	61.1	0.799	47.8	0.793
thiophene	93.2	0.847	71.4	0.827	55.8	0.805

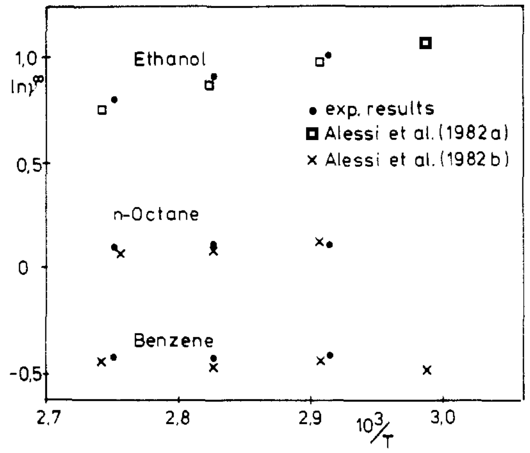

Figure 1. Activity coefficients γ^∞ of ethanol, *n*-octane, and benzene on the stationary phase 10-nonadecanone.

From the data in Table V and VI and Figure 1 it can be seen that there is good agreement between our results and the results of Parcher (*6*) and Alessi et al. (*7*, *8*).

Discussion

Apart from the actual values obtained, these measurements also afford information regarding the temperature dependence of the boundary activity coefficients of the various substances.

Table III. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for the Stationary Phase of 10-Nonadecanone ($C_{19}H_{38}O$)

	70.1 °C		80.5 °C		90.1 °C	
	V_g^0	γ^∞	V_g^0	γ^∞	V_g^0	γ^∞
n-pentane	30.8	0.983	24.0	0.977	19.4	0.970
n-heptane	187.5	1.077	133.5	1.067	99.5	1.061
n-octane	455.1	1.119	308.3	1.112	220.5	1.106
isooctane	174.4	1.152	126.6	1.133	95.3	1.126
cyclohexane	136.5	0.829	101.0	0.817	77.6	0.812
methylcyclohexane	242.7	0.868	174.2	0.860	130.4	0.856
1-hexene	72.6	0.931	54.5	0.925	42.7	0.917
1-octene	429.1	1.012	293.2	1.006	209.7	1.009
methanol	25.0	2.616	20.1	2.238	15.4	2.154
ethanol	40.4	2.787	29.4	2.531	23.1	2.261
1-propanol	101.7	2.433	70.0	2.244	52.5	2.029
2-propanol	56.3	2.444	40.9	2.168	30.8	1.988
1-butanol	262.7	2.299	175.2	2.088	124.0	1.921
tert-butanol	72.2	1.913	52.2	1.730	39.1	1.611
1-pentanol	666.3	2.015	421.9	1.879	286.3	1.767
3-methyl-1-butanol	509.3	2.058	328.8	1.884	226.6	1.747
methyl acetate	42.1	1.305	32.5	1.240	25.5	1.216
ethyl acetate	86.1	1.197	63.2	1.173	48.3	1.153
propyl acetate	206.7	1.160	144.8	1.131	106.7	1.106
butyl acetate	506.2	1.106	339.0	1.088	238.9	1.080
ethyl propionate	196.8	1.100	137.0	1.089	102.0	1.063
ethyl butyrate	437.1	1.007	295.4	1.009	209.9	1.014
vinyl acetate	71.7	1.242	53.3	1.200	41.7	1.152
acetone	38.6	1.382	29.8	1.325	23.9	1.278
2-butanone	95.3	1.166	70.1	1.135	53.7	1.110
2-pentanone	212.3	1.111	150.0	1.088	110.9	1.072
3-pentanone	223.8	1.048	157.3	1.030	115.0	1.026
4-methyl-2-pentanone	340.7	1.094	234.4	1.079	170.5	1.064
4-heptanone			669.6	1.095	462.5	1.081
n-butanal	91.5	1.047	67.6	1.035	52.0	1.029
2-methylpropanal	65.8	1.033	49.5	1.011	38.9	0.990
n-pentanal	231.7	1.044	163.3	1.024	120.6	1.009
crotonaldehyde	179.8	1.295	126.9	1.268	96.1	1.218
furfurol			641.6	2.552	444.9	2.396
benzene	168.6	0.661	122.6	0.650	93.3	0.649
toluene	434.5	0.686	297.4	0.694	216.4	0.696
o-xylene			860.9	0.728	592.6	0.736
m-xylene			717.3	0.734	499.2	0.739
p-xylene			704.3	0.723	493.3	0.725
chlorobenzene			624.4	0.656	441.9	0.657
1-bromopropane	123.2	0.680	90.1	0.681	70.0	0.670
thiophene	191.7	0.663	138.8	0.656	104.0	0.657
tetrachloromethane	148.8	0.671	107.4	0.683	83.1	0.679

On the nonpolar stationary phase *n*-octacosane, the polar components in particular exhibit a marked temperature dependence: thus the activity coefficients of the alcohols decrease greatly with increasing temperature. This effect is not so marked for esters, ketones, and aldehydes, but is still noticeable. A comparison of these results with compiled information on heats of mixing (DECHEMA Chemistry Data Series (*9*)) confirms these findings. A decrease of the activity coefficients with increasing temperature means in thermodynamic terms that the partial molar excess enthalpies at infinite dilution $\bar{h}_i^{E\infty}$ have positive values. The following relation applies

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial 1/T}\right)_P = \frac{\bar{h}_i^{E\infty}}{R} \tag{3}$$

where $\bar{h}_i^{E\infty}$ is the partial molar excess enthalpy at infinite dilution of component i.

With the assumption that $\bar{h}_i^{E\infty}$ is constant across the small temperature range considered, the equation can be integrated directly:

$$\bar{h}_i^{E\infty} = R\,\frac{T_1T_2}{T_1 - T_2}\ln\frac{\gamma_2^\infty}{\gamma_1^\infty} \tag{4}$$

Table VII contains the partial molar excess enthalpies obtained by using eq 4 for some substances measured on 1-octacosane

Table IV. Experimental Retention Volumes and Activity Coefficients at Infinite Dilution for the Stationary Phase 1-Eicosene ($C_{20}H_{40}$)

	55.9 °C		64.6 °C		75.4 °C	
	V_g^0	γ^∞	V_g^0	γ^∞	V_g^0	γ^∞
n-pentane	43.8	1.024	35.5	0.991	27.3	0.976
n-heptane	309.7	1.106	229.9	1.075	158.9	1.067
isooctane	277.8	1.205	207.8	1.176	146.7	1.158
cyclohexane	215.3	0.851	165.6	0.823	119.9	0.807
methylcyclohexane	399.4	0.883	299.8	0.856	209.6	0.848
1-hexene	104.5	1.010	81.6	0.983	60.1	0.972
methanol	28.2	4.083	22.3	3.643	15.9	3.420
ethanol	53.3	3.940	40.2	3.555	28.0	3.260
1-propanol	142.7	3.463	103.2	3.120	69.5	2.834
2-propanol	81.0	3.285	60.1	2.944	41.7	2.646
1-butanol	395.4	3.264	276.2	2.918	174.8	2.681
tert-butanol	111.0	2.384	81.8	2.160	55.9	1.994
methyl acetate	49.8	1.709	40.2	1.635	30.4	1.550
ethyl acetate	110.4	1.562	85.3	1.472	62.3	1.397
propyl acetate	283.9	1.503	211.6	1.413	146.6	1.351
ethyl propionate	277.7	1.372	202.2	1.329	140.9	1.276
vinyl acetate	80.0	1.842	62.9	1.718	46.8	1.615
acetone	40.1	2.080	32.7	1.941	25.0	1.836
2-butanone	106.8	1.729	83.1	1.624	61.1	1.540
2-pentanone	254.2	1.621	191.3	1.527	135.0	1.453
3-pentanone	268.6	1.528	201.3	1.443	141.9	1.374
4-methyl-2-pentanone			310.9	1.501	214.2	1.432
n-butanal	99.6	1.559	78.3	1.471	57.5	1.426
2-methylpropanal	71.2	1.519	56.6	1.434	42.7	1.370
n-pentanal	274.4	1.541	204.0	1.468	143.3	1.403
crotonaldehyde	182.8	2.219	139.6	2.065	100.4	1.929
benzene	216.0	0.844	165.6	0.813	120.2	0.790
toluene	608.7	0.853	445.6	0.827	305.9	0.811
1-bromopropane	146.3	0.919	113.8	0.883	84.0	0.855
thiophene	233.6	0.902	177.6	0.868	128.7	0.836
tetrachloromethane	207.2	0.774	159.0	0.753	115.3	0.743

Table V. Comparison of Activity Coefficients Data in *n*-Octacosane

	our results				Parcher et al. (1975)	
	80.2 °C γ^∞	100.3 °C γ^∞	120.2 °C γ^∞	av γ^∞	av γ^∞	diff, %
n-pentane	0.693	0.688	0.694	0.692	0.698	–0.87
n-heptane	0.744	0.751	0.757	0.751	0.768	–2.26
n-octane	0.774	0.798	0.794	0.789	0.796	–0.89
n-decane	0.833	0.864	0.858	0.852	0.845	0.82

Table VI. Comparison of Activity Coefficients in 10-Nonadecanone

	γ^∞	$\gamma^{\infty a}$	γ^∞	$\gamma^{\infty a}$	γ^∞	$\gamma^{\infty a}$
temp, °C	70.1	70.7	80.5	80.5	90.1	89.6
n-pentane	0.983	1.00	0.977	0.99	0.970	0.96
n-heptane	1.077	1.10	1.067	1.04	1.061	1.03
n-octane	1.119	1.13	1.112	1.09	1.106	1.07
1-hexene	0.931	0.92	0.925	0.92	0.917	0.90
1-octene	1.012	1.00	1.006	0.99	1.009	0.98
benzene	0.661	0.64	0.650	0.64	0.649	0.64
temp, °C	70.1	70.6	80.5	80.8	90.1	91.5
methyl acetate	1.305	1.24	1.240	1.21	1.216	1.18
ethyl acetate	1.197	1.17	1.173	1.14	1.153	1.13
propyl acetate	1.160	1.09	1.131	1.12	1.106	1.08
butyl acetate	1.106	1.04	1.088	1.03	1.080	1.01
ethanol	2.787	2.71	2.531	2.42	2.261	2.12
1-propanol	2.433	2.25	2.244	2.06	2.029	1.90

[a] Alessi et al. (1982) (ref *7*, *8*).

Table VII. Partial Molar Excess Enthalpy[a] at Infinite Dilution $\bar{h}_i^{E\infty}$ (J/mol) for the Stationary Phases *n*-Octacosane and 1-Docosanol

	$\bar{h}_i^{E\infty}$	
	octacosane	docosanol
n-pentane	–42	2175
n-heptane	–500	907
n-octane	–737	560
isooctane	–107	1537
n-decane	–854	
cyclohexane	–151	319
methylcyclohexane	–860	1075
1-hexene	–200	934
1-octene	–74	1665
ethanol	18495	1133
1-propanol	15912	733
2-propanol	16585	726
1-butanol	17077	1821
tert-butanol	15488	230
1-pentanol	15778	
3-methyl-1-butanol	15693	780
1-hexanol	15175	
1-heptanol	16405	
1-octanol	16639	
methyl acetate	5243	6651
ethyl acetate	3852	5317
propyl acetate	4300	4778
butyl acetate	3773	4007
ethyl propionate	3414	3663
ethyl butyrate	2426	2108
vinyl acetate	4842	8013
acetone	7262	5427
2-butanone	5423	6238
2-pentanone	4239	5250
3-pentanone	4116	4418
4-methyl-2-pentanone	4615	4371
4-heptanone	4019	3314
2-octanone	5417	
n-butanal	3315	
2-methylpropanal	4423	
n-pentanal	4450	1799
crotonaldehyde	7334	6435
furfurol	13748	11674
benzene	1185	1902
toluene	1094	2117
o-xylene	739	1441
m-xylene	331	1619
p-xylene	–42	1582
chlorobenzene	1622	2110
1-bromopropane	2411	3512
tetrachloromethane	398	424
thiophene	3344	2860

[a] For temperature range see Tables I and II.

and 1-docosanol. The activity coefficients of the nonpolar alkanes and alkenes in the mixtures with 1-octacosane are practically temperature-independent and the partial molar excess enthalpies are very small. In mixtures with the polar stationary phase 1-docosanol, the boundary activity coefficients of the alkanes and alkenes also decrease slightly with increasing temperature. The temperature dependence of the polar and somewhat polar components decreases in comparison to the values on *n*-octacosane. The polar alcohols on 1-docosanol show the lowest temperature dependence, while on *n*-octacosane they exhibit the largest temperature dependence.

The activity coefficient at infinite dilution is, as already mentioned, not measured directly but calculated from other measured parameters (see eq 1 and 2). Thus the error in γ^∞ must be obtained from the law of propagation of errors. The following measured parameters can exhibit errors and must be taken into account in the error calculation with their corresponding standard deviations: difference between retention time and dead time $t_R - t_A$, 0.02 min; volume flow of carrier gas F (the quantity measured is the time taken by a soap bubble to traverse a volume of 20 mL), 0.2 s; mass of stationary phase m_L (relative), 2%; pressure at column entrance p_A, 0.001 bar; pressure at column exit p_E, 0.003 bar; temperature at flow meter T_{fm}, 0.2 K; oven temperature, 0.2 K. The results obtained by using a computer program can be summarized as follows: the errors in the determination of the volume flow of the carrier gas, of the pressure at column entrance and exit, and of the temperature at the flow meter are negligible. The main source of error in the calculation of the specific retention volume corrected to 0 °C is the measurement of the weight of stationary phase in the column (2%). In addition there is a small error from the determination of the difference between retention time and dead time: this is dependent on the size of the difference and decreases with incrasing time difference. This was taken into account for the measurements by choosing the gas-chromatographic conditions to be such that the difference $t_R - t_A$ was not too small. However, it must also be taken into consideration that the half-width of the peaks increases with increasing time. This in turn causes the determination of the retention time to be less exact. The total error in the determination of the specific retention volume is about

$$s_{V_g^0} = 2.5\%$$

Apart from this deviation, the error in measurement of the oven temperature also affects the determination of the activity coefficient at infinite dilution. The resulting error in γ^∞, taking into account the fact that the Antoine constants taken from the literature and used in the calculation of the saturation vapor pressure are also subject to error, is

$$s_{\gamma^\infty} = 3.0\%$$

Measurements with different masses of stationary phase or flow rates lead to results within this error range.

Conclusion

GLC allows the fast and accurate determination of activity coefficients at infinite dilution for high boiling stationary phases. By use of careful temperature control and saturation of the carrier gas this method can also be used for stationary phases with appreciable vapor pressures. Results for *N*-methylpyrrolidone and *N*-formylmorpholine will be presented in part 2. The results obtained were used for the development of a modified UNIFAC method (*10*).

Acknowledgment

We thank Prof. Dr. U. Onken for his supporting interest in this work.

Glossary

F	gas flow
$\bar{h}_i^{E\infty}$	partial molar excess enthalpy of component i at infinite dilution
M_L	molecular weight of the stationary phase
m_L	mass on stationary phase
P	total pressure
p_A	pressure at column exit
p_E	pressure at column entrance
p_{fm}	pressure at the flow meter
P_i^s	vapor pressure of component i
P_w	vapor pressure of water
R	gas constant
s	experimental error
T	temperature
t_A	dead time
T_{fm}	temperature at flow meter, K
t_R	retention time
V_g^0	specific retention volume (corrected at 0 °C)
γ_i^∞	activity coefficient at infinite dilution of component i
φ_i^s	fugacity coefficient of component i in the saturation state

Literature Cited

(1) Laub, R. J.; Pecsok, R. L. *Physicochemical Applications of Gas Chromatography*; Wiley: New York, 1978.
(2) Leroi, J. C.; Masson, J. C.; Renon, H.; Fabries, J. F.; Sannier, H. *Ind. Eng. Chem. Process Des. Dev.* **1977**, *16*, 139.
(3) Tiegs, D.; Gmehling, J.; Medina, A. G.; Bastos, J.; Soares, M.; Alessi, P.; Kikic, I. *Activity Coefficients at Infinite Dilution*, 2 parts; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, 1986.
(4) Soave, G. *Chem. Eng. Sci.* **1972**, *27*, 1197.
(5) Graboski, M. S.; Daubert, T. E. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 443.
(6) Parcher, J. F.; Weiner, P. H.; Hussey, C. L.; Westlake, T. N. *J. Chem. Eng. Data* **1975**, *20*, 145.
(7) Alessi, P.; Kikic, I.; Alessandrini, A.; Fermeglia, M. *J. Chem. Eng. Data* **1982**, *27*, 445.
(8) Alessi, P.; Kikic, I.; Nonino, C.; Visalberghi, M. O. *J. Chem. Eng. Data* **1982**, *27*, 448.
(9) Christensen, C.; Gmehling, J.; Rasmussen, P.; Weidlich, U. *Heats of Mixing Data Collection*; DECHEMA Chemistry Data Series; DECHEMA: Frankfurt, 1984.
(10) Weidlich, U.; Gmehling, J. *Ind. Eng. Chem. Research*, in press.

Received for review July 10, 1986. Accepted December 24, 1986. We thank "Deutsche Forschungsgemeinschaft", "Arbeitsgemeinschaft Industrieller Forschungsvereinigungen", and "Fonds der Chemischen Industrie" for financial support.