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Measurement of Activity Coefficients at Infinite Dilution Using Differential Ebulliometry and Non-Steady-State Gas–Liquid Chromatography

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Differential ebulliometry and non-steady-state gas–liquid chromatography have been used to measure activity coefficients at infinite dilution for 31 binary systems containing alkanes, ketones, and alcohols over the temperature range 303–343 K. A comparison between the results obtained with these two methods shows that differential ebulliometry provides more reliable results for the systems with a relative volatility lower than 15. Non-steady-state gas–liquid chromatography can however readily be used as an alternative to conventional gas–liquid chromatography for the measurement of activity coefficients at infinite dilution in low-boiling solvents.

Introduction

Activity coefficients at infinite dilution (γ^∞) are of great interest not only from the theoretical point of view but also for the practicing chemist and chemical engineer. This parameter characterizes the behavior of a dissolved material (the solute) which is completely surrounded by solvent molecules. Values of limiting activity coefficients are important not only for the development of new thermodynamic models but also for the adjustment of reliable model parameters or the choice of selective solvents for extractive rectification, extraction, or absorption.

This paper deals with a comparison of the results provided by two different methods for measuring activity coefficients at infinite dilution. Differential ebulliometry and non-steady-state gas–liquid chromatography were used to measure γ^∞ values for 31 binary systems containing alkanes (*n*-pentane, *n*-hexane, *n*-heptane), alcohols (methanol, ethanol), and ketones (acetone, 2-butanone) in the temperature range 303–343 K.

Apparatus and Experimental Procedure

(a) *Differential Ebulliometry.* The method used for the measurement of γ^∞ values was that proposed by Trampe and Eckert (*1*), who provided a detailed description of a similar apparatus and the measurement procedure.

The experimental setup for the measurement of activity coefficients at infinite dilution is shown schematically in Figure 1. Several ebulliometers are arranged in series so as to make possible the simultaneous determination of γ^∞ values of various compounds in one solvent. The temperature measurement is not absolute; the value for an ebulliometer filled with pure solvent is compared with that for a second ebulliometer containing the corresponding solution. Pressure variations in the system lead to a variation of the boiling point in each ebulliometer. Measurement of the temperature difference reduces the effect of the pressure changes to a large extent but not completely.

The total pressure is measured and controlled by a system manufactured by MKS Baratron Instruments consisting of a Baratron 390 HA transducer sensor head, a Baratron 250 controller, and a Baratron 270 conditioner. Dry air can enter the system via an automatically controlled needle valve. The various components of the apparatus are linked via tubes and connected to a vacuum pump by a needle valve. In addition a 50-L ballast tank is included between the vacuum pump and the rest of the system in order to improve the pressure stability. The system pressure is indicated on a digital display with a resolution of 0.1 mmHg; it is kept constant within between 0.1 and 0.2 mmHg during the complete measurement cycle. The pressure variations are dependent on the total pressure and the boiling behavior of the solvent. An improved pressure control would increase the temperature stability in the system. The temperature was measured by a Hewlett-Packard quartz thermometer, model 2804 A, the temperature difference measured within 0.0001 K. The boiling part of the ebulliometer is vacuum jacketed, and the cooling medium (methanol) in the condenser is at 243 K.

The ebulliometers stand on magnetic heater/stirrers (IKA-MAG RH), which have a dual function. They have to heat the contents of the ebulliometers to their boiling points and compensate the heat losses occurring during the experiments, and furthermore they allow high-speed stirring (up to 2000 rpm). This is required in order to achieve a thorough mixing of the components and thus to permit the thermodynamic equilibrium to be reached as rapidly as possible. In addition they prevent the occurrence of bumping.

All the ebulliometers (a maximum of five) are filled gravimetrically with ca. 300 cm^3 of the same solvent. After the required pressure value is reached, heat is applied until a steady-state boiling condition is reached. A temperature sensor is placed in the reference ebulliometer and kept there throughout the experiment. The other temperature sensor is introduced into the first measurement ebulliometer. The temperature difference ΔT is noted when "equilibrium" has been reached between the two ebulliometers, which at this stage are still filled with pure solvent. This initial temperature difference is less than 0.01 K and is mainly due to errors in the calibration of the two sensors; it is later subtracted from the measured ΔT values. The sensor is then introduced into the second ebulliometer. An aliquot (0.5–3 cm^3) of the pure solute or of a known mixture of solute and solvent is injected into the first measurement ebulliometer with the help of a syringe via a septum. The exact amount of the solute or the mixture is determined by weighing the syringe before and after the injection. The temperature difference between the measurement and the reference ebulliometer is measured after equilibrium has been reached (ca. 30 min). During the experiment solute is injected four to six times into each

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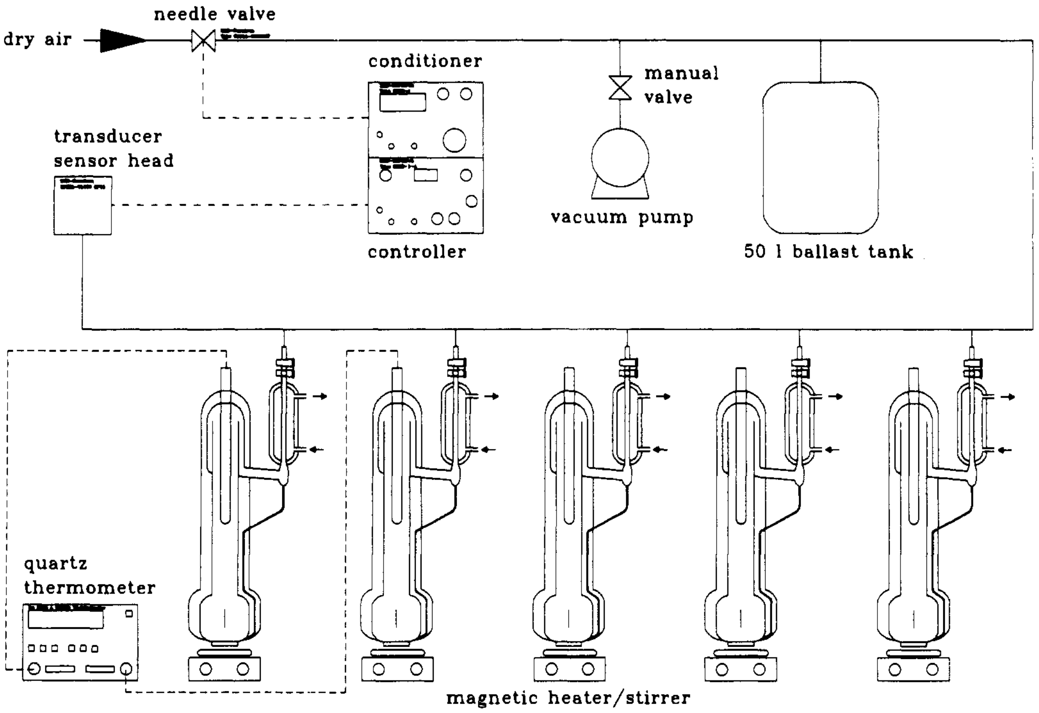

Figure 1. Experimental setup used to measure limiting activity coefficients by ebulliometry.

measurement ebulliometer. The time required to determine γ^∞ for four solutes at a given pressure is between 8 and 10 h.

The system was used successfully for pressures between 100 mmHg and atmospheric pressure. At lower pressures a pressure variation of a particular magnitude, caused by the nature of the vapor pressure curve as a function of temperature, has a greater effect on the temperature than that at higher pressures. The applicable temperature range seems to be ca. 5 K above room temperature and the calibration range of the quartz thermometer. At temperatures near and below room temperature the vapor is superheated, so that unstable and unreliable temperature differences are observed.

This method is suited best for systems for which the relative volatility at infinite dilution lies between 0.1 and 15. If the solvent is more volatile than the solute, the γ^∞ value is extremely sensitive to the limiting slope. If the solute is considerably more volatile than the solvent, the corrections for the proportion of the solute in the vapor phase and the magnitude of the liquid holdup in the ebulliometer become very important.

Further details of ebulliometer development, the design of the system, and the measurement procedure are to be found in Dallinga's (*2*) diploma thesis.

(b) Non-Steady-State Gas–Liquid Chromatography. Gas–liquid chromatography is one of the fastest and most reliable techniques for the measurements of activity coefficients at infinite dilution in high-boiling solvents (*3*). The following data are required for the determination of γ^∞: net retention time, carrier gas velocity, column entrance and exit pressure, and exact amount of stationary phase on the support. This means that the mass loss during the experiment must be kept as low as possible by means of extremely good thermostating, presaturation of the carrier gas by the solvent, and the minimization of the pressure decrease across the column. Several researchers have estimated the relative error in the activity coefficient at infinite dilution to be ca. 3% for high-boiling solvents.

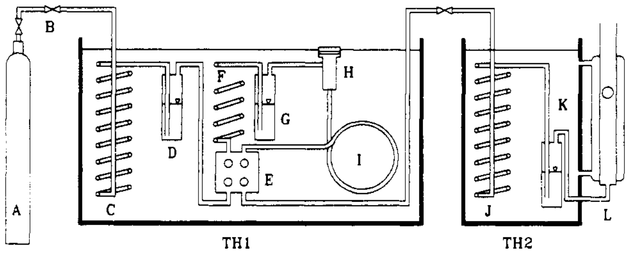

Figure 2. Schematic of the experimental apparatus for the measurement of limiting activity coefficients by non-steady-state gas–liquid chromatography: A, carrier gas supply; B, needle valve; C, heating coil; D, G, K, saturators; E, thermal conductivity detector; F, J, tempering coils; H, injection block; I, chromatographic column; L, soap bubble flowmeter; TH1, TH2, thermostats.

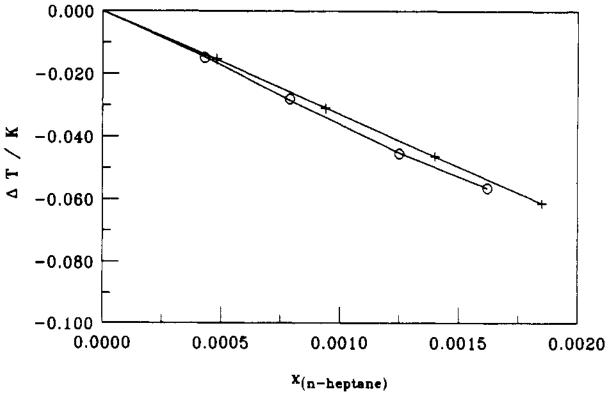

Figure 3. Temperature difference ΔT as a function of the solute mole fraction x for the system *n*-heptane in 2-butanone: —, calculated values; T = 313.13 K (γ^∞ = 4.404), +, experimental values; T = 313.12 K (γ^∞ = 4.416), ○, experimental values.

Knoop et al. (*4*) show that in the case of lower-boiling solvents such as *N*-formylmorpholine, 1-pentanol, *m*-xylene, or toluene the relative error in the determination of γ^∞ increases to 3–7%; i.e., the relative error in the solvent mass determination, and thus the relative error in the γ^∞ values, increases with increasing solvent vapor pressures. When the mass loss becomes too great, it is possible to replace the "classical" GLC technique by a non-steady-state GLC (NSS-GLC). This method was first investigated by Belfer and Locke

(*5*), and is based on the following concept: solvent (0.5–1.5 cm^3) is injected at constant column temperature and carrier gas velocity onto a column filled with uncoated inert carrier material (between 1.5 and 5 g of Chromosorb PAW DMCS, 60–80 mesh). The solvent condenses in a uniform manner on the carrier material and reaches equilibrium with the carrier gas. The solvent is removed from the column throughout the experiment. Under these experimental conditions the mass loss of the solvent decreases linearly with time.

For the experimental investigation we have developed and built our own gas chromatograph (*6*) (Figure 2), which has been described in detail by Knoop et al. (*4*).

Data Reduction

(a) *Ebulliometry.* The following expression was used for the determination of γ_i^∞ values from the experimentally measured ΔT–x data for a highly dilute solution:

$$\gamma_1^\infty = \frac{\varphi_1^{(P_2^s)}\left[P_2^s - \left\{1 - \frac{P_2^s v_2}{RT} + \frac{P_2^s}{\varphi_2^s}\left(\frac{\partial \varphi_2}{\partial P}\right)_T\right\}\frac{dP_2^s}{dT}\left(\frac{\partial T}{\partial x_1}\right)_P^\infty\right]}{\varphi_1^s P_1^s \exp[v_1(P_2^s - P_1^s)/RT]} \qquad (1)$$

The (saturation) fugacity coefficients in eq 1 were calculated with the help of the Soave–Redlich–Kwong equation of state, and the saturation pressure was calculated using the Antoine equation. The necessary parameters for the pure substances were obtained from the Dortmunder Datenbank DDB (*7*). The quantity determined experimentally is $(\partial T/\partial x_1)_P^\infty$, the limiting slope of the isobaric ΔT–x data. To obtain the slope, the experimental ΔT–x data are fitted to various empirical equations (quadratic, cubic, van Laar). A typical example of a plot of ΔT against the composition x is shown in Figure 3. The complete evaluation of the raw data to provide the activity coefficient at infinite dilution has been described in detail by Trampe and Eckert (*1*). The derivation of eq 1 used for the calculation of the γ_i^∞ values from differential ebulliometry is described in detail by Arlt (*8*).

The limits of applicability of the ebulliometric technique are determined by the relative volatility at infinite dilution (α_{12}^∞):

$$\alpha_{12}^\infty = \gamma_1^\infty P_1^s / P_2^s \qquad (2)$$

Our investigations have demonstrated that the ebulliometer type used has an upper limit such that $\alpha_{12}^\infty < 15$. Above this value the reproducibility of the γ_i^∞ values becomes significantly worse.

(b) *Non-Steady-State Gas–Liquid Chromatography (NSS-GLC).* The following procedure was used to obtain the γ_i^∞ values from experimental data: the quantity determined experimentally is $dt_N/d\theta$, the retention differential parameter and characteristic NSS-GLC value for a given solute in a solvent under isothermal conditions.

A given amount of solute is injected at time $t = t_1$ and leaves the column at the retention time $t = t_{N1}$. At a later time ($t = t_2$) the injection of the solvent is repeated. The solute now requires a lower retention time t_{N2} to travel through the column. Using the expressions $dt_N = t_{N2} - t_{N1}$ and $d\theta = t_2 - t_1$, the retention differential parameter is defined as the ratio $dt_N/d\theta$. The activity coefficient at infinite dilution can be calculated using eq 3; this means that, apart from the

$$\gamma_1^\infty = \frac{\varphi_2^s P_2^s}{\varphi_1^s P_1^s}\frac{d\theta}{dt_N} \qquad (3)$$

retention differential parameter, the saturation fugacity coefficient φ_i^s and the saturation vapor pressure P_i^s must also be known. Since the exact mass of the stationary phase is not required for the determination of the γ^∞ value, the main problem arising from the classical GLC technique does not exist for NSS-GLC.

During our experiments we found that the optimum liquid loading range lies between 10% and 30% and is thus very similar to that used in classical GLC.

The solvent injection is repeated several times during the experiment in order to compensate random errors such as slight variations in the temperature or the velocity of the carrier gas. In Figure 4 the net retention times are plotted against the injection times for the solutes *n*-pentane and *n*-hexane in 2-butanone at 323.15 K. The retention differential parameter required for the calculation is obtained from these data with the help of linear regression methods.

The saturation fugacity coefficients and the saturation vapor pressures are calculated as described above for the ebulliometric method. The derivation of eq 3 used for the calculation of the γ_i^∞ values from NSS-GLC is described in detail by Belfer and Locke (*5*).

From classical GLC the problem of adsorption effects is well known. Using the NSS-GLC technique, adsorption phenomena tend to cancel, since retention time differences are measured.

Materials

The solutes, and in particular the solvents, used in this work were >99.9% pure as determined by GLC with a FID detector. All chemicals were used as purchased, dried, and stored over 3A molecular sieves. The water content was determined using the Karl-Fischer method. The following chemicals were used: acetone, p.a., Riedel-de Haën or Janssen, 0.018 wt % H_2O; 2-butanone, Fluka, 0.017 wt % H_2O; methanol, p.a., Janssen, 0.019 wt % H_2O; ethanol, p.a., Riedel-de Haën, 0.019 wt % H_2O; *n*-pentane, p.a., Merck, H_2O not detectable; *n*-hexane, p.a., J. T. Baker B. V. "baker analyzed" or Merck, H_2O not detectable; *n*-heptane, p.a., Merck, H_2O not detectable.

Results

Activity coefficients at infinite dilution were measured in the temperature range 303–353 K with the help of the slightly modified ebulliometer design by Trampe and the NSS-GLC technique developed by Belfer. Alkane–alcohol systems could not be studied by differential ebulliometry, since these systems showed $\alpha_{12}^\infty > 15$ in the chosen temperature range. The same is also true for the system acetone–*n*-heptane.

All systems studied in this work show positive deviations from Raoult's law and a decrease in γ^∞ with increasing temperature; i.e., the partial molar excess enthalpies at infinite dilution of the systems are endothermic in the temperature range studied. The mean γ^∞ values are given in Table I. The estimated relative error for the ebulliometric method is always below 3%. The estimates are based on repeated measurements, standard deviations of the experimentally determined limiting slopes, and the sensitivity of the γ^∞ values to the slope and the liquid holdup correction. The estimated relative error of the NSS-GLC method is based on repeated measurements and a Gauss error propagation calculation and lies between 3.5% and 5%.

The results obtained in this work are compared in Table I with those reported by other researchers. It can be seen that the agreement with the literature data is good, the deviation generally lying within the estimated error range. A comparison with literature results is possible for all systems studied except for the two systems acetone in *n*-pentane and *n*-heptane in 2-butanone.

Table I. Experimental Activity Coefficients at Infinite Dilution γ_i^∞ Obtained by Differential Ebulliometry and Non-Steady-State Gas–Liquid Chromatography and Comparison to Literature Data

		ebulliometry			NSS-GLC		literature			
solvent	solute	pressure (kPa)	temp (K)	γ_i^∞	temp (K)	γ_i^∞	temp (K)	γ_i^∞	method[a]	ref
n-pentane	acetone	81.97	303.12	7.07						
n-pentane	2-butanone	81.97	303.12	5.19			298.15	5.470	HSGC	12
n-hexane	acetone	23.22	301.46	6.21						
							301.90	6.120	EBUL	1
		25.14	303.39	6.17						
					313.15	5.78				
					323.15	5.04				
					333.15	4.55				
							341.95	3.909	EBUL	13
n-hexane	2-butanone						297.95	4.380	EBUL	14
							298.15	4.530	HSGC	12
		25.14	303.39	4.31						
		37.36	313.27	3.92	313.15	3.98				
					323.15	3.69				
							315.15	3.970	EBUL	14
							331.95	3.600	EBUL	14
							340.25	3.400	EBUL	14
n-hexane	methanol						263.15	392.000	DILU	15
							273.15	243.000	DILU	15
							283.15	136.000	DILU	15
					315.15	55.8	313.15	77.200	DILU	15
					333.25	39.1				
							341.20	34.400	EBUL	1
n-hexane	ethanol						297.15	62.600	DILU	16
							297.35	58.200	DILU	16
							297.65	59.400	DILU	16
							298.15	55.350	HSGC	12
							304.75	38.000	EBUL	14
					313.15	32.5				
							316.55	37.600	DILU	16
							316.65	35.400	DILU	16
							322.55	23.000	EBUL	14
					333.25	23.0	333.95	21.900	DILU	16
							333.95	22.400	DILU	16
							351.45	14.700	DILU	16
							351.55	14.800	DILU	16
n-heptane	acetone						309.15	6.310	GCLR	17
					323.15	5.10				
					333.15	4.59				
					343.15	4.27	343.15	3.580	EBUL	18
							353.15	3.720	EBUL	18
							363.15	3.900	EBUL	18
							373.15	4.100	EBUL	18
n-heptane	2-butanone						298.15	4.260	HSGC	12
		12.29	312.89	4.23	313.15	4.12	313.15	4.080	GCLR	19
		27.92	332.99	3.27			333.15	3.320	GCLR	19
					343.15	3.12				
n-heptane	methanol						263.15	234.000	DILU	15
							273.15	173.000	DILU	15
							283.15	80.000	GCLR	20
							293.15	114.000	DILU	15
							298.15	40.600	HENR	21
							309.15	56.100	GCLR	17
					313.15	51.9	313.15	67.700	DILU	15
					323.15	38.5	323.15	18.300	EBUL	18
					333.15	28.0	333.15	15.600	EBUL	18
							343.15	13.200	EBUL	18
							353.15	11.000	EBUL	18
							363.15	9.200	EBUL	18
							373.15	7.800	EBUL	18
n-heptane	ethanol						293.15	51.000	GCLR	20
							298.15	47.500	HENR	21
							298.15	49.220	HSGC	12
							309.15	36.000	GCLR	17
					313.15	43.1	313.15	39.940	EBUL	30
							314.45	36.300	DILU	16
							314.55	34.600	DILU	16
					323.15	32.6	323.15	17.300	EBUL	18
							332.15	23.200	DILU	16
					333.15	23.8	333.15	16.000	EBUL	18
							333.15	16.270	EBUL	30
							343.15	14.700	EBUL	18
							349.55	14.600	DILU	16
							349.55	15.100	DILU	16

Table I. (Continued)

		ebulliometry			NSS-GLC		literature			
solvent	solute	pressure (kPa)	temp (K)	γ_i^∞	temp (K)	γ_i^∞	temp (K)	γ_i^∞	method[a]	ref
n-heptane	ethanol						353.15	13.300	EBUL	18
							363.15	12.200	EBUL	18
							366.75	9.800	DILU	16
							373.15	11.200	EBUL	16
acetone	*n*-pentane	37.81	303.11	5.84	303.15	5.77				
							308.15	5.290	RADM	22
		68.31	318.23	4.51						
		81.94	323.20	4.29						
acetone	*n*-hexane						298.15	6.500	GLCN	23
							300.90	6.410	EBUL	1
		37.78	303.10	6.51	303.15	6.78				
							306.90	6.240	EBUL	1
							308.15	6.440	EBUL	24
							308.15	6.500	RADM	22
		56.58	313.22	5.68						
							316.70	5.540	EBUL	1
							318.15	5.850	EBUL	24
							323.15	5.620	EBUL	24
							324.40	5.240	EBUL	1
							328.15	5.350	EBUL	24
							328.40	4.950	EBUL	1
							329.34	5.392	EBUL	13
							333.15	5.100	GLCN	23
							373.15	4.500	GLCN	23
acetone	*n*-heptane	37.82	303.12	7.63	313.15	7.81				
		56.48	313.17	7.33	313.15	7.35	313.15	6.350	EBUL	18
							323.15	6.130	EBUL	18
							333.15	5.910	EBUL	18
acetone	methanol	37.92	313.20	2.11						
		46.68	308.23	1.99						
		56.48	313.24	1.93			313.15	1.900	EBUL	18
							323.15	1.800	EBUL	18
							329.15	1.710	EBUL	25
							329.30	1.720	EBUL	31
							329.34	1.753	EBUL	13
							329.34	1.775	EBUL	13
							333.15	1.730	EBUL	18
acetone	ethanol						298.30	2.440	EBUL	1
		38.12	303.23	2.32						
							306.75	2.240	EBUL	14
							308.20	2.240	EBUL	1
		56.68	313.20	2.09						
							315.15	2.120	EBUL	14
							318.30	2.070	EBUL	1
							327.35	1.920	EBUL	14
							328.50	1.920	EBUL	1
							329.34	1.741	EBUL	13
2-butanone	*n*-pentane						293.15	3.660	GCLR	20
					303.15	3.76				
					313.15	3.56				
					323.15	3.43				
2-butanone	*n*-hexane						298.15	4.000	GLCN	23
							298.15	4.300	GCLR	20
					303.15	4.27				
		23.73	313.08	3.98	313.15	4.12				
					323.15	3.82				
					333.15	3.65				
							333.15	3.150	GLCN	23
							373.15	2.600	GLCN	23
2-butanone	*n*-heptane				303.15	4.66				
		23.80	313.13	4.41	313.15	4.41				
					323.15	4.16				
		51.93	333.05	3.93	333.15	3.90				
2-butanone	methanol				303.15	2.42				
		23.57	312.93	2.24	313.15	2.22	314.65	2.290	EBUL	14
		51.92	333.07	2.16			333.25	2.090	EBUL	14
2-butanone	ethanol						298.15	2.360	HSGC	12
		23.57	312.93	2.24	313.15	2.18	314.65	2.260	EBUL	14
					323.15	2.10				
		46.58	333.07	1.98			333.25	1.990	EBUL	14
							348.55	1.740	EBUL	14
							352.74	1.747	EBUL	13
methanol	*n*-pentane						298.15	19.500	NSGC	26
					303.15	20.3				
					313.15	18.5				

Table I. (Continued)

		ebulliometry			NSS-GLC		literature			
solvent	solute	pressure (kPa)	temp (K)	γ_i^∞	temp (K)	γ_i^∞	temp (K)	γ_i^∞	method[a]	ref
methanol	*n*-hexane						263.15	34.400	DILU	15
							273.15	31.700	DILU	15
							293.15	27.800	DILU	15
							298.00	27.000	GLCN	23
					303.15	25.9				
					313.15	23.5	313.15	24.200	DILU	15
							333.15	19.000	GLCN	23
							373.15	13.500	GLCN	23
methanol	*n*-heptane						263.15	46.000	DILU	15
							273.15	44.000	DILU	15
							293.15	37.100	DILU	15
					303.15	35.1				
					313.15	31.7	313.15	33.900	EBUL	18
							313.15	34.100	DILU	15
							323.15	29.700	EBUL	18
							333.15	25.200	EBUL	18
							343.15	23.600	EBUL	18
methanol	acetone						298.15	2.160	NSGC	26
					303.15	2.11				
		27.94	308.13	2.04						
		35.52	313.17	2.01	313.15	2.00	313.15	2.000	EBUL	18
							323.15	1.910	EBUL	18
							333.15	1.890	EBUL	18
							337.60	1.770	EBUL	31
							337.65	1.720	EBUL	25
							337.65	1.880	EBUL	27
							337.65	1.890	EBUL	27
							337.65	1.910	EBUL	27
							337.79	1.828	EBUL	13
							337.79	1.979	EBUL	13
							343.15	1.830	EBUL	18
methanol	2-butanone						298.15	2.490	HSGC	12
					303.15	2.32				
		27.93	308.14	2.26			308.60	2.270	EBUL	1
					313.15	2.22				
		44.61	318.21	2.20			318.15	2.210	EBUL	1
							328.50	2.110	EBUL	1
							337.00	2.070	EBUL	1
ethanol	*n*-pentane						293.15	9.600	GCLR	20
							298.15	9.490	NSGC	26
							299.65	8.900	DILU	16
					303.15	9.25	304.15	9.100	DILU	16
							310.35	8.700	DILU	16
							312.05	8.600	DILU	16
					313.15	8.76	313.15	8.270	RADM	22
							321.95	8.500	DILU	16
					323.15	8.25	322.15	8.300	DILU	16
							324.65	8.300	DILU	16
							335.15	8.200	DILU	16
							342.95	7.800	DILU	16
							352.35	7.000	DILU	16
							354.15	6.900	DILU	16
							354.35	7.400	DILU	16
ethanol	*n*-hexane						293.15	12.000	GCLR	20
							298.15	11.000	NSGC	28
							298.15	12.000	GLCN	23
					303.15	12.7				
					313.15	11.6	313.15	9.900	RADM	22
							318.15	10.800	GLCN	29
							322.15	10.000	DILU	16
							323.15	10.600	GLCN	29
							333.15	9.700	GLCN	23
							350.85	8.100	EBUL	14
							354.15	8.700	DILU	16
							373.15	8.400	GLCN	23
ethanol	*n*-heptane				303.15	15.0				
					313.15	14.1	313.15	13.000	EBUL	18
							313.15	13.900	GCLR	19
							313.15	15.340	EBUL	30
							319.35	11.800	EBUL	14
							322.15	12.000	DILU	16
					323.15	13.3	323.15	12.000	EBUL	18
							333.15	11.000	EBUL	18
							333.15	14.210	EBUL	30
							335.15	10.900	EBUL	14

Table I. (Continued)

		ebulliometry			NSS-GLC		literature			
solvent	solute	pressure (kPa)	temp (K)	γ_i^∞	temp (K)	γ_i^∞	temp (K)	γ_i^∞	method[a]	ref
ethanol	*n*-heptane						337.65	11.200	DILU	16
							343.15	10.200	EBUL	18
							347.75	10.300	EBUL	14
							351.10	11.100	EBUL	31
							353.15	9.800	EBUL	18
							354.15	10.800	DILU	16
ethanol	acetone						293.15	2.380	GCLR	20
							299.15	2.650	NSGC	28
					303.15	2.70				
		18.92	314.23	2.43	313.15	2.50				
		23.21	318.50	2.35			318.15	2.090	GLCN	29
		29.17	322.95	2.22	323.15	2.30	322.45	2.170	EBUL	14
							323.15	2.160	GLCN	29
							335.75	2.030	EBUL	14
							348.25	1.920	EBUL	14
							351.47	1.725	EBUL	13
ethanol	2-butanone						298.15	2.450	HSGC	12
					303.15	2.57				
		18.65	313.85	2.28	313.15	2.31				
					323.15	2.22				
							351.47	1.973	EBUL	13

[a] Experimental techniques: GCLR, gas–liquid chromatography with gas-phase correction; EBUL, ebulliometry; DILU, dilutor technique (gas stripping technique); HSGC, headspace chromatography; GLCN, gas–liquid chromatography with no specification of gas-phase correction; HENR, calculated from Henry coefficients; NSGC, non-steady state gas–liquid chromatography; RADM, Rayleigh distillation method.

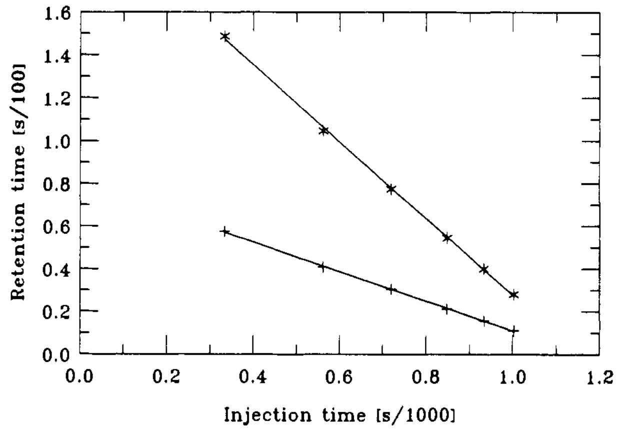

Figure 4. Retention differentials for the solutes *n*-pentane and *n*-hexane in the solvent 2-butanone at 323.15 K: —, fitted with linear regression; solute *n*-pentane (γ^∞ = 3.43), +, experimental values; solute *n*-hexane (γ^∞ = 3.82), *, experimental values.

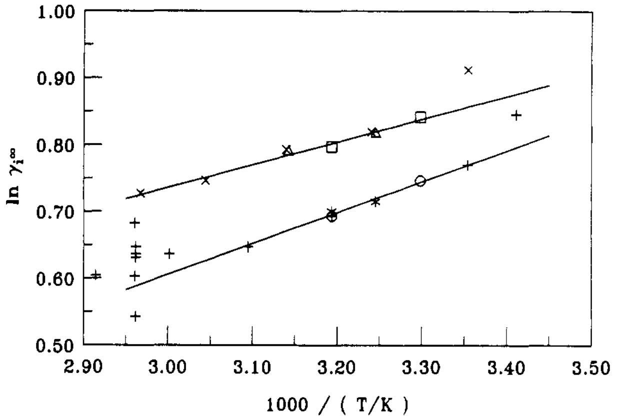

Figure 5. Temperature dependence of the limiting activity coefficients γ_i^∞ of acetone and 2-butanone in the solvent methanol: +, *, ○, solute acetone; ×, △, □, solute 2-butanone; +, ×, published γ^∞ values; *, △, γ^∞ values measured with differential ebulliometry (this work); ○, □, γ^∞ values measured with non-steady-state GLC (this work).

Greater deviations from the literature values are only observed for the systems *n*-heptane in acetone and acetone in *n*-heptane. In the latter case the published γ^∞ values increase with increasing temperature. It can however be shown with the help of published excess enthalpy values (*9*) that the temperature dependence obtained from the published γ^∞ values must be incorrect.

A comparison with the literature values for the solutes acetone and 2-butanone in methanol as solvent is shown in Figure 5 as a function of temperature.

The activity coefficients at infinite dilution determined in the present work have in part been used for the fitting of group interaction parameters of the modified UNIFAC method (Dortmund) (*10, 11*).

If the partial molar excess enthalpy at infinite dilution ($\bar{h}_i^{E,\infty}$) is known, it is possible to extrapolate to other temperatures. The following relationship can be derived with the help of the Gibbs–Helmholtz equation:

$$(\partial \ln \gamma_i^\infty / \partial(1/T))_{P,x} = \bar{h}_i^{E,\infty}/R \qquad (4)$$

If we assume for the sake of simplicity that $\bar{h}_i^{E,\infty}$ is constant within a certain temperature interval, it is possible to integrate eq 4. $\bar{h}_i^{E,\infty}$ values were determined with the help of linear regression using the measured γ^∞ values from Table I and are given in Table II. The uncertainty in these values depends on the values of the slopes. The confidence interval (95% probability) is estimated as follows: for $\bar{h}_i^{E,\infty}$ = 2000–5000 J/mol, the uncertainty is approximately 35%; for $\bar{h}_i^{E,\infty}$ = 5000–10000 J/mol, the uncertainty is approximately 30%; for $\bar{h}_i^{E,\infty}$ > 10000 J/mol, the uncertainty is approximately 15%.

A comparison with experimentally determined $\bar{h}_i^{E,\infty}$ values was not possible for the systems studied in this work. We thus attempted to obtain the required quantity with the help of "finite" excess enthalpy values. The $\bar{h}_i^{E,\infty}$ values were calculated by fitting the h^E data (mean temperature as γ^∞ data) using the Redlich–Kister, respectively SSF, equation (*10*).

The mean deviation between the $\bar{h}_i^{E,\infty}$ values determined from γ^∞ values and those from h^E values is ca. 25%. The $\bar{h}_i^{E,\infty}$ values determined in two different ways are shown in Figure 6 for the system 2-butanone in methanol. The dotted line

Table II. Calculated Partial Molar Excess Enthalpies at Infinite Dilution $\bar{h}^{E,\infty}$ of Solutes in Solvents

solvent	solute	$\bar{h}^{E,\infty}$ [a] (J/mol)	$\bar{h}^{E,\infty}$ [b] (J/mol)
n-hexane	acetone	8367 (301–333 K)	8990 (308 K)
n-hexane	2-butanone	6380 (303–323 K)	7200 (298 K)
n-heptane	acetone	8201 (323–343 K)	8267 (298 K)
n-heptane	2-butanone	9053 (313–343 K)	7838 (318 K)
n-heptane	methanol	26747 (313–333 K)	28436 (333 K)
n-heptane	ethanol	25731 (313–333 K)	25855 (323 K)
acetone	*n*-pentane	12652 (303–323 K)	9260 (293 K)
acetone	methanol	7060 (303–313 K)	3375 (298 K)
2-butanone	*n*-pentane	3747 (303–323 K)	4350 (298 K)
2-butanone	*n*-hexane	4453 (303–333 K)	7221 (298 K)
2-butanone	*n*-heptane	4959 (303–333 K)	7838 (318 K)
2-butanone	methanol	2833 (303–333 K)	2842 (323 K)
2-butanone	ethanol	4706 (313–333 K)	4705 (313 K)
methanol	acetone	3856 (303–313 K)	3655 (323 K)
methanol	2-butanone	2830 (303–318 K)	3948 (313 K)
ethanol	*n*-pentane	4655 (303–323 K)	6802 (298 K)
ethanol	*n*-heptane	4899 (303–323 K)	3972 (323 K)
ethanol	acetone	7387 (303–323 K)	5302 (323 K)
ethanol	2-butanone	6071 (303–323 K)	4554 (308 K)

[a] Calculated by linear regression of experimental γ^{∞} values from Table I. [b] Calculated from literature (*9*) experimental excess enthalpies.

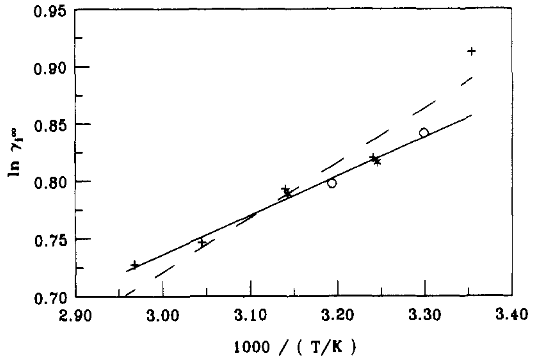

Figure 6. Temperature dependence of the limiting activity coefficients γ_i^{∞} of the system 2-butanone in the solvent methanol: +, published γ^{∞} values; *, γ^{∞} values measured with differential ebulliometry (this work); ○, γ^{∞} values measured with non-steady state GLC (this work); - - -, slope calculated from finite h^E values; —, slope fitted with linear regression from experimental γ^{∞} values (this work).

represents the value obtained from h^E data. The solid line was derived with the help of linear regression from the experimental values (asterisks and circles) obtained in this work. The literature values for activity coefficients at infinite dilution are also shown (denoted by plus signs).

It should be noted when making such a comparison that between three and four values were generally used in the determination of $\bar{h}_i^{E,\infty}$ values from γ^{∞} values. In the case where $\bar{h}_i^{E,\infty}$ values are obtained from h^E data the concentration range generally lies between $0.05 \le x_i \le 0.95$; i.e., no information on conditions close to infinite dilution is used in fitting the parameters. A more useful comparison would be possible with the help of excess enthalpies which were actually measured at infinite dilution.

Conclusion

Activity coefficients at infinite dilution have been measured for 31 binary systems (alkane–alcohol, alkane–ketone, and alcohol–ketone) in the temperature range 303–343 K. The values obtained from differential ebulliometry and non-steady-state GLC generally agree well with the literature data.

The ebulliometer design used provides extremely reliable values for relative volatilities < 15. The NSS-GLC technique is suitable for all systems for which the solute has a greater volatility than the solvent. The estimated relative deviations of the NSS-GLC method (3.5–5%) are however larger than those of the ebulliometric method (<3%). NSS-GLC provides an extremely valuable alternative to the extension of the classical GLC method for the rapid determination of γ^{∞} values.

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Glossary

h^E	excess enthalpy, J/mol
$\bar{h}_i^{E,\infty}$	partial molar excess enthalpy at infinite dilution, J/mol
P	total pressure, kPa
P_i^s	saturation vapor pressure of component *i*, kPa
R	universal gas constant, J/(mol K)
T	temperature, K
ΔT	temperature difference, K
v_i	liquid molar volume, cm³/mol
x_i	mole fraction of component *i* in the liquid phase
y_i	mole fraction of component *i* in the vapor phase
α_{ij}^{∞}	relative volatility at infinite dilution of component *i* in *j*
γ_i	activity coefficient of component *i*
γ_i^{∞}	activity coefficient at infinite dilution of component *i*
$d\theta/dt_N$	retention differential parameter
φ_i^s	fugacity coefficient of component *i* in the saturation state

Subscripts

1	solute
2	solvent

Registry Numbers Supplied by Author. *n*-Pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; methanol, 67-56-1; ethanol, 64-17-5; acetone, 67-64-1; 2-butanone, 78-93-3.

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