Measurement of Activity Coefficients at Infinite Dilution Using Gas−Liquid Chromatography. 5. Results for *N*-Methylacetamide, *N*,*N*-Dimethylacetamide, *N*,*N*-Dibutylformamide, and Sulfolane as Stationary Phases

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Activity coefficients at infinite dilution are reported for more than 40 solutes (alkanes, alcohols, ketones, aromatic hydrocarbons, halocarbons, esters, nitriles, aldehydes, ethers, furan, pyridine, and water) in four selective solvents (*N*-methylacetamide, *N*,*N*-dimethylacetamide, *N*,*N*-dibutylformamide and sulfolane) at 303, 318, and 333 K. These values were measured with the help of gas−liquid chromatography (GLC) and show a good agreement when comparing them with various activity coefficients at infinite dilution taken from the literature. The temperature dependence found in the GLC experiments could be confirmed using excess enthalpy data. An important application of the present data can be seen in the selection of a suitable solvent for selective separation processes such as azeotropic and extractive distillation or extraction, where it is usually sufficient to know the ratio of the limiting activity coefficients of the components to be separated (selectivity at infinite dilution) in order to determine the selective effect of a given solvent. Furthermore the data will be used to extend the range of application for existing group contribution methods (e.g. modified UNIFAC) for the synthesis and design of separation processes.

Introduction

The separation of systems with separation factors near or equal to unity requires the use of additives which are also known as entrainers. In the case of extractive distillation the entrainer is added in order to influence the activity coefficients of the substances to be separated to a different extent. The ratio of the activity coefficients of the components to be separated is denoted as the selectivity.

$$S_{ij} = \gamma_i/\gamma_j \tag{1}$$

In the synthesis and design of distillation processes the relative volatility of two components, also known as the separation factor (in the simplified form)

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^s}{\gamma_j P_j^s} \tag{2}$$

is more useful, since with the help of additional information on the saturation vapor pressures it permits a prediction of the possible distillate and bottom product compositions. Simplifying assumptions are that the fugacity coefficients in the vapor phase and in the saturation state (φ_i^V and φ_i^s) often have similar values and the Poynting correction shows values close to unity for low to moderate pressure differences $P - P_i^s$ (Gmehling and Kolbe, 1992). In many cases it is sufficient to know the separation factor at infinite dilution ($(\alpha_{ij})_k^\infty = \gamma_i^\infty P_i^s/\gamma_j^\infty P_j^s$) in order to be able to estimate how selective the effect of an additive on the activity coefficients in the liquid mixture and thus on the separability of the systems will be.

The aim of the measurements carried out in this work is to find entrainer candidates for extractive distillation to which previously little or no attention has been paid. Thus solvents have been chosen for which no or few data were previously available, but whose suitability (selective function) has already been shown in other applications, for example in other thermal separation processes (e.g. liquid−liquid extraction). A further goal is the extension of the database for the development of group contribution methods, e.g. modified UNIFAC (Dortmund) (Weidlich and Gmehling, 1987; Gmehling et al., 1993). The present data can be used in the future to describe systems with functional groups which are to be found, for example, in alkylated acetamides, alkylated formamides, or sulfolane.

In a systematic study the activity coefficients at infinite dilution have been experimentally determined for more than 40 substances in four solvents, in order to obtain quantitative information for the selection of the additive which is the most suitable for the problem at hand. The results of this study allow a judgement as to the selectivity of a solvent for a given separation problem and in addition provide further important information for a reliable design of the separation process.

Measurement Procedure

The solid support used for all stationary phases (selective solvents) was Chromosorb P-AW-DMCS (60−80 mesh). The coating of the predried carrier material with the solvent was carried out with methanol (solubilizer) in a rotary evaporator. After removal of the solubilizer, the column (length 200 mm, inner diameter 4.1 mm) was carefully filled with the coated solid support and the liquid loading (i.e. the amount of stationary phase or solvent on the inert carrier material) was determined gravimetrically. The apparatus used in these investigations was developed in our laboratory. A detailed scheme of the homemade gas chromatograph, the description of the measurement procedure, and the most important equations for evaluation purposes together with theoretical explanations are given by Knoop et al. (1989). The following four selective solvents were examined: *N*-methylacetamide (C_3H_7NO), *N*,*N*-dimethylacetamide (C_4H_9NO), *N*,*N*-dibutylformamide ($C_9H_{19}NO$), and sulfolane ($C_4H_8SO_2$).

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Table 1. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent *N*-Methylacetamide as a Function of Temperature *T*

solute i	303 K	318 K	333 K
pentane	11.96 (303.37)	11.37 (318.37)	10.85 (333.21)
hexane	15.24 (302.97)	13.89 (318.37)	12.73 (333.76)
heptane	18.51 (303.08)	17.05 (318.37)	16.03 (333.24)
cyclohexane		9.312 (318.37)	8.840 (333.24)
methylcyclohexane	12.01 (303.08)	11.07 (318.37)	10.64 (333.20)
cyclohexene	7.108 (303.02)	6.388 (318.37)	6.344 (333.21)
methanol	0.696 (303.21)	0.705 (318.36)	0.715 (332.76)
ethanol	0.904 (303.37)	0.872 (318.36)	0.851 (332.76)
2-propanol	0.992 (303.24)	0.959 (318.36)	0.934 (333.34)
1-butanol	1.270 (303.08)	1.096 (318.42)	0.971 (333.20)
2-methyl-1-propanol		1.013 (318.42)	0.970 (333.21)
allyl alcohol		0.574 (318.43)	0.631 (331.90)
acetone	2.098 (303.37)	2.015 (318.37)	1.918 (333.21)
2-butanone	2.237 (303.08)	2.179 (318.37)	2.106 (333.21)
4-methyl-2-pentanone	3.478 (303.24)	3.395 (318.36)	3.231 (333.34)
benzene	3.522 (303.32)	3.335 (318.36)	2.984 (333.34)
toluene	3.808 (303.21)	3.706 (318.36)	3.618 (333.20)
ethylbenzene	5.077 (303.10)	4.933 (318.36)	4.818 (331.90)
chlorobenzene			3.064 (332.76)
dichloromethane	1.022 (303.32)	1.036 (318.36)	1.051 (333.20)
chloroform	0.563 (303.10)	0.734 (318.36)	0.752 (333.08)
tetrachloromethane	2.988 (304.16)	3.146 (318.36)	3.293 (331.90)
1,2-dichloroethane	1.601 (303.37)	1.620 (318.36)	1.638 (333.20)
trichloroethylene	2.180 (303.37)	2.303 (318.36)	2.433 (333.21)
methyl formate		2.127 (318.37)	2.190 (331.90)
methyl acetate		2.464 (318.37)	2.436 (331.90)
ethyl acetate	2.792 (304.16)	2.764 (318.37)	2.723 (331.90)
propyl acetate	3.286 (304.16)	3.178 (318.37)	3.045 (333.24)
butyl acetate	3.550 (303.02)	3.549 (318.37)	3.457 (333.21)
acetonitrile	2.138 (303.08)	2.017 (318.37)	1.927 (333.21)
acetaldehyde	2.108 (303.08)	2.031 (318.37)	1.918 (333.21)
isobutyraldehyde	2.751 (303.08)	2.636 (318.37)	2.537 (333.20)
diethyl ether	4.188 (303.21)	4.120 (318.36)	4.060 (333.21)
diisopropyl ether	6.665 (303.08)	6.479 (318.37)	6.338 (333.20)
methyl *tert*-butyl ether	4.775 (303.32)	4.442 (318.37)	4.182 (333.20)
ethyl *tert*-butyl ether[a]	6.257 (303.37)	6.106 (318.37)	5.967 (333.08)
isopropyl *tert*-butyl ether[a]	7.500 (303.37)	7.486 (318.37)	7.186 (333.08)
methyl *tert*-amyl ether	5.603 (303.37)	5.431 (318.37)	5.179 (333.08)
tetrahydrofuran	2.125 (303.08)	2.089 (318.37)	2.057 (333.08)
1,4-dioxane	2.485 (303.02)	2.422 (318.36)	2.302 (333.34)
furan	1.770 (304.16)	1.832 (318.37)	1.946 (331.90)
pyridine		1.525 (318.36)	1.582 (331.90)
water[b]		0.743 (318.43)	0.872 (331.90)

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$. [b] After correction of the observed adsorption effects (Jönsson and Mathiasson, 1979).

In all cases the purities of the solvents were higher than 99.8% (GLC analysis of peak areas, CP-Wax 52 column, temperature 150 °C, FID detector). Results for more than 40 solutes (alkanes, alcohols, ketones, aromatics, chloroalkanes, esters, aldehydes, ethers, nitriles, furan, pyridine, and water) were obtained at 303, 318, and 333 K. Since GLC is itself a separation technique, the results are not influenced by small solute impurities. Thus commercially available substances were used for the investigations without further purification.

The determination of γ^∞ requires the following information: the net retention time of the solute, the measuring temperature, column inlet and outlet pressures, the carrier gas flow rate, and the amount of the stationary phase on the solid support. From these experimentally determined parameters the specific net retention volume V_g^0 corrected to 0 °C is calculated in order to evaluate the measurements. The activity coefficient at infinite dilution is then given by

$$\gamma_i^\infty = \frac{273.15R}{V_g^0 \varphi_i^s P_i^s M_L} \tag{3}$$

where R is the gas constant, M_L is the molar mass of the solvent, and P_i^s is 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 solute φ_i^s is calculated according to the Soave−Redlich−Kwong equation of state (Gmehling and Kolbe, 1992); the required critical data and acentric factors are again taken from the DDB. The net retention time is equal to the difference between the retention time of the solute (solute peak) and the dead time (peak caused by the air which is injected together with the solute). The net retention time is a measure of the partition of the solute between the gas (mobile) phase and the stationary phase (solvent). This partitioning is determined directly by the phase equilibrium behavior. The relative amount of the stationary phase (liquid loading: 15−30%) and the sample volumes of the injected solutes (0.05−0.5 μL) were varied in order to be able to detect possible adsorption effects; however, these latter were only observed in the case of water. The method proposed by Jönsson and Mathiasson (1979) was used to account for the retention caused by adsorption of water and to obtain the corrected γ^∞ values (based on distribution between the liquid and the vapor phase).

Subsequent to a series of measurements the amount of solvent (stationary phase) on the inert carrier material is determined gravimetrically. This is done by removing the coated solid support from the column, mixing it, and

Table 2. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent *N*,*N*-Dimethylacetamide as a Function of Temperature *T*

solute i	303 K	318 K	333 K
pentane	7.955 (303.56)	6.856 (317.62)	5.889 (333.41)
hexane	9.767 (303.21)	8.227 (317.62)	6.936 (333.30)
heptane	11.60 (303.21)	9.798 (317.62)	8.278 (333.41)
cyclohexane	6.543 (303.56)	6.201 (317.62)	5.902 (333.41)
methylcyclohexane	8.261 (303.21)	7.439 (317.62)	6.842 (333.20)
cyclohexene	6.103 (303.21)	5.609 (317.63)	5.168 (333.41)
methanol	0.422 (303.56)	0.435 (317.62)	0.463 (333.41)
ethanol	0.531 (303.56)	0.580 (317.62)	0.628 (333.55)
2-propanol	0.603 (303.21)	0.578 (317.62)	0.554 (333.20)
1-butanol			0.786 (333.41)
2-methyl-1-propanol			0.702 (333.41)
allyl alcohol		0.709 (317.56)	0.420 (333.41)
acetone	1.097 (303.56)	1.031 (317.62)	0.966 (333.41)
2-butanone			1.382 (333.55)
4-methyl-2-pentanone	1.440 (303.21)	1.328 (317.63)	1.223 (333.20)
benzene	1.143 (303.56)	1.166 (317.62)	1.189 (333.55)
toluene	1.485 (303.56)	1.466 (317.62)	1.447 (333.20)
ethylbenzene	2.073 (303.56)	1.968 (317.62)	1.874 (333.20)
chlorobenzene		3.308 (317.62)	
dichloromethane	0.321 (303.56)	0.360 (317.63)	0.403 (332.99)
chloroform	0.178 (303.21)	0.217 (317.56)	0.274 (333.20)
tetrachloromethane	0.949 (303.21)	1.231 (317.58)	1.616 (333.55)
1,2-dichloroethane	0.544 (303.56)	0.634 (317.58)	0.747 (333.41)
trichloroethylene	0.848 (303.56)	0.923 (317.58)	1.013 (332.99)
methyl formate	1.113 (303.33)	1.192 (317.56)	1.274 (332.99)
methyl acetate	1.474 (303.33)	1.229 (317.62)	1.020 (333.55)
ethyl acetate	1.810 (303.33)	1.648 (317.62)	1.498 (333.55)
propyl acetate	2.013 (303.33)	1.874 (317.58)	1.748 (332.99)
butyl acetate	2.367 (303.33)	2.031 (317.58)	1.742 (333.20)
acetonitrile	0.688 (303.21)	0.691 (317.62)	0.694 (333.41)
acetaldehyde	0.940 (303.21)	0.912 (317.62)	0.882 (333.41)
isobutyraldehyde	1.260 (303.21)	1.213 (317.62)	1.168 (333.99)
diethyl ether	3.235 (303.44)	3.177 (317.62)	3.129 (333.55)
diisopropyl ether	4.043 (303.21)	3.704 (317.62)	3.401 (332.99)
methyl *tert*-butyl ether	2.900 (303.56)	2.474 (317.62)	2.100 (332.99)
ethyl *tert*-butyl ether[a]	4.024 (303.56)	3.869 (317.62)	3.726 (333.55)
isopropyl *tert*-butyl ether[a]	4.855 (303.56)	4.637 (317.62)	4.423 (333.55)
methyl *tert*-amyl ether	3.486 (303.56)	3.371 (317.62)	3.268 (333.55)
tetrahydrofuran	1.529 (303.33)	1.496 (317.58)	1.463 (333.55)
1,4-dioxane	1.329 (303.33)	1.292 (317.56)	1.255 (333.55)
furan	0.685 (303.33)	0.848 (317.56)	1.053 (333.41)
pyridine	0.638 (303.39)	0.822 (317.56)	1.048 (332.99)

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$.

weighing it into porcelain crucibles in samples of 0.4−1 g. The solvent is then evaporated from the solid support for several hours in a muffle furnace at 500 °C. However, under the stated conditions the pure uncoated Chromosorb suffers from a loss of weight due to the removal of strongly adsorbed water, which has been taken into consideration, too. The hygroscopic character of the solvent *N*,*N*-dimethylacetamide, which leads to a very high degree of retention, did not permit determination of the γ^∞ values for water. This behavior also made the gravimetric determination of the amount of stationary phase more difficult, since the absorption of moisture from the air on emptying the column indicated values which were too high. We attempted to reduce this influence as far as possible when making measurements with *N*,*N*-dimethylacetamide by removing the solvent directly from the column. This was done by heating the latter in a stream of inert gas (argon) 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 the column treatment. A control crucible experiment with the prepared carrier and a muffle furnace showed that the stationary phase had been removed quantitatively. The whole procedure allowed us to determine the amount of stationary phase as the difference between the masses of the column when containing loaded and unloaded carrier material.

Results and Discussion

Tables 1−4 contain the results for the four selective solvents at three temperatures (303, 318, and 333 K); the exact temperature of the measurement is given in brackets after the γ^∞ value. Figure 1 shows as an example the linear relationship between the natural logarithm of the activity coefficients at infinite dilution ($\ln \gamma_i^\infty$) and the inverse of the absolute temperature for six different ethers in *N*,*N*-dibutylformamide. The decrease in the activity coefficients on going from ethers with relatively high molecular weights (e.g. isopropyl *tert*-butyl ether, $M = 116.20$) via the series of ethers with shorter alkyl chains (diisopropyl ether, ethyl *tert*-butyl ether, methyl *tert*-amyl ether, $M = 102.18$) to those of low molecular weight (e.g. diethyl ether, $M = 74.12$) is also visible; however, as is shown by the γ^∞ values for methyl *tert*-butyl ether ($M = 88.15$) and diethyl ether, this is not always the case. The observation that the limiting activity coefficients of the symmetrically substituted ethers (diisopropyl ether and diethyl ether) lie between those for two unsymmetrically substituted ethers, which are, in addition, sterically more demanding, indicates that the molecular shape has an influence on the mechanism of retention too.

Table 3. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent *N*,*N*-Dibutylformamide as a Function of Temperature *T*

solute i	303 K	318 K	333 K
pentane	2.482 (302.81)	2.365 (318.32)	2.271 (332.43)
hexane	2.751 (302.81)	2.581 (318.32)	2.446 (332.43)
heptane	3.047 (302.81)	2.797 (318.32)	2.665 (332.43)
cyclohexane	2.126 (302.81)	1.974 (318.32)	1.889 (332.43)
methylcyclohexane	2.309 (302.81)	2.148 (318.32)	2.021 (332.43)
cyclohexene	1.592 (302.81)	1.528 (318.32)	1.476 (332.43)
methanol	0.785 (302.81)	0.783 (318.33)	0.791 (332.43)
ethanol	0.829 (302.81)	0.837 (318.33)	0.845 (332.43)
2-propanol		0.814 (318.33)	0.796 (332.43)
1-butanol			0.718 (332.46)
2-methyl-1-propanol		0.628 (318.33)	0.655 (332.46)
allyl alcohol	0.451 (302.81)		0.541 (332.43)
acetone	1.095 (302.81)	1.046 (318.32)	1.026 (332.43)
2-butanone	0.952 (302.81)	0.962 (318.32)	0.969 (332.43)
4-methyl-2-pentanone	1.079 (302.81)	1.049 (318.33)	1.040 (332.46)
benzene	0.822 (302.81)	0.844 (318.33)	0.861 (332.43)
toluene	0.922 (302.81)	0.952 (318.33)	0.976 (332.43)
ethylbenzene		1.104 (318.33)	1.101 (332.46)
chlorobenzene	4.730 (302.81)	4.137 (318.33)	3.703 (332.43)
dichloromethane	0.324 (302.81)	0.342 (318.33)	0.364 (332.43)
chloroform	0.159 (302.81)	0.191 (318.33)	0.223 (332.43)
tetrachloromethane	0.890 (302.81)	0.902 (318.33)	0.919 (332.43)
1,2-dichloroethane	0.507 (302.81)	0.511 (318.33)	0.524 (332.43)
trichloroethylene	0.569 (302.81)	0.588 (318.33)	0.616 (332.43)
methyl formate	1.165 (302.81)	1.204 (318.33)	1.237 (332.43)
methyl acetate	1.310 (302.81)	1.272 (318.32)	1.234 (332.43)
ethyl acetate	1.355 (302.81)	1.282 (318.32)	1.235 (332.43)
propyl acetate	1.375 (302.81)	1.290 (318.32)	1.257 (332.46)
butyl acetate	1.291 (302.81)	1.270 (318.32)	1.251 (332.46)
acetonitrile	1.166 (302.81)	1.132 (318.33)	1.118 (332.43)
acetaldehyde	1.011 (302.81)	0.949 (318.33)	0.924 (332.43)
isobutyraldehyde	1.003 (302.81)	0.973 (318.33)	0.964 (332.43)
diethyl ether	1.465 (302.81)	1.432 (318.32)	1.412 (332.46)
diisopropyl ether	1.917 (302.81)	1.808 (318.32)	1.772 (332.43)
methyl *tert*-butyl ether	1.417 (302.81)	1.380 (318.32)	1.350 (332.43)
ethyl *tert*-butyl ether[a]	1.836 (302.81)	1.714 (318.32)	1.651 (332.43)
isopropyl *tert*-butyl ether[a]	2.025 (302.81)	1.884 (318.33)	1.807 (332.43)
methyl *tert*-amyl ether	1.531 (302.81)	1.446 (318.32)	1.418 (332.43)
tetrahydrofuran	0.877 (302.81)	0.874 (318.33)	0.872 (332.43)
1,4-dioxane	1.197 (302.81)	1.081 (318.33)	1.059 (332.43)
furan	0.680 (302.81)	0.694 (318.33)	
pyridine	0.634 (302.81)	0.743 (318.33)	0.784 (332.46)
water[b]	3.041 (302.81)	2.868 (318.33)	2.780 (332.46)

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$. [b] After correction of the observed adsorption effects (Jönsson and Mathiasson, 1979).

A comparison between the data of a solute in *N*-methylacetamide and *N*,*N*-dimethylacetamide shows that the activity coefficients at infinite dilution are generally lower in the dimethyl derivative. This tendency is confirmed by series of measurements and values reported by other authors (Tiegs et al., 1986). No γ^∞ values could be determined for water as the solute in *N*,*N*-dimethylacetamide due to the hygroscopic character of the solvent, which led to an extremely high degree of retention. Figure 2 shows the γ^∞ values for benzene and toluene in sulfolane. Apart from the values determined in this work the data for the corresponding systems obtained by other authors [Gaile et al. (1974), Rawat et al. (1976), and Schiller (1989)] are also shown. The comparison demonstrates that there is good agreement between the present data and those taken from the literature.

The process which is clearly the most liable to error when γ^∞ is measured with the help of gas−liquid chromatography is the determination of the mass of the stationary phase. In the case of the systems used here the inexactitude of the gravimetric determination has an effect of on average 3% on the γ^∞ value. The reproducibility of the data is, however, much better (ca. 1%).

The temperature dependence of the γ^∞ values is important for the choice of the best temperature for the use of the selective solvent. A graph of ln γ^∞ versus the inverse absolute temperature often shows a straight line in a limited temperature interval. According to Gibbs−Helmholtz the value for the partial molar excess enthalpy at infinite dilution can be obtained from the slope of this line (Gmehling and Kolbe, 1992):

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

In the great majority of the solutes studied it is clear that the limiting activity coefficients tend toward ideal behavior ($\gamma_i = 1$) as the temperature increases. For components with γ^∞ values greater than unity this implies a decrease of the activity coefficient ($\bar{H}_i^{E,\infty} > 0$) and for components with γ^∞ values less than unity an increase of the activity coefficient with increasing temperature ($\bar{H}_i^{E,\infty} < 0$). Figure 3 shows as an example the temperature dependence of the limiting activity coefficients of toluene and propyl acetate in *N*-methylacetamide. The activity coefficient at infinite dilution decreases with increasing temperature, so that positive values of the partial molar excess enthalpies can be expected; h^E measurements carried out with an isothermal flow calorimeter (Gmehling, 1993) show that the temperature dependence determined from the direct measurement

Table 4. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞, for the Solvent Sulfolane as a Function of Temperature *T*

solute i	303 K	318 K	333 K
pentane	34.63 (303.37)	30.44 (317.90)	27.26 (332.60)
hexane	46.99 (303.81)	41.08 (317.90)	35.98 (332.81)
heptane	62.02 (303.37)	54.00 (317.90)	47.37 (332.60)
cyclohexane	28.10 (303.58)	21.20 (317.90)	16.06 (333.18)
methylcyclohexane	38.71 (303.58)	32.37 (317.90)	24.94 (332.81)
cyclohexene	13.09 (303.81)	11.45 (317.90)	10.34 (333.74)
methanol	2.336 (303.81)	2.082 (317.90)	1.867 (333.74)
ethanol	3.304 (303.78)	2.893 (317.90)	2.338 (332.81)
2-propanol	4.346 (303.78)	3.602 (317.90)	2.863 (332.81)
1-butanol	5.354 (303.10)	4.494 (317.90)	3.700 (333.60)
2-methyl-1-propanol	4.660 (303.78)	4.016 (317.90)	3.239 (332.81)
allyl alcohol	1.645 (303.10)	1.609 (317.90)	1.574 (333.60)
acetone	1.617 (303.78)	1.544 (317.90)	1.466 (334.19)
2-butanone	1.994 (303.10)	1.949 (317.90)	1.910 (332.60)
4-methyl-2-pentanone	3.894 (303.78)	3.770 (317.90)	3.625 (333.60)
benzene	2.378 (303.81)	2.347 (317.90)	2.315 (333.74)
toluene	3.613 (303.78)	3.492 (317.90)	3.357 (333.60)
ethylbenzene	5.323 (303.10)	4.932 (317.90)	4.436 (332.60)
chlorobenzene	2.691 (303.81)	2.595 (317.90)	2.465 (332.81)
dichloromethane	0.901 (303.78)	0.940 (317.90)	0.980 (334.19)
chloroform	0.934 (303.10)	0.974 (317.90)	1.006 (332.60)
tetrachloromethane	4.602 (303.28)	4.583 (317.90)	4.564 (333.74)
1,2-dichloroethane	1.132 (303.10)	1.167 (317.90)	1.208 (333.60)
trichloroethylene	3.264 (303.10)	3.092 (317.90)	2.943 (332.60)
methyl formate	1.434 (303.81)	1.421 (317.90)	1.408 (333.74)
methyl acetate	1.946 (303.81)	1.912 (317.90)	1.878 (333.74)
ethyl acetate	2.782 (303.10)	2.670 (317.90)	2.514 (332.60)
propyl acetate	3.662 (303.10)	3.504 (317.90)	3.365 (332.60)
butyl acetate	4.988 (303.10)	4.671 (317.90)	4.452 (334.19)
acetonitrile	1.063 (303.78)	1.070 (317.90)	1.077 (334.19)
acetaldehyde	1.436 (303.10)	1.383 (317.90)	1.333 (333.60)
isobutyraldehyde	2.559 (303.28)	2.358 (317.90)	2.188 (332.70)
diethyl ether	6.590 (303.81)	6.409 (317.90)	6.208 (333.60)
diisopropyl ether	14.45 (303.81)	13.50 (317.90)	12.57 (334.19)
methyl *tert*-butyl ether	7.317 (303.81)	7.155 (317.90)	6.894 (333.60)
ethyl *tert*-butyl ether[a]	12.84 (303.81)	12.23 (317.90)	11.09 (333.74)
isopropyl *tert*-butyl ether[a]	17.69 (303.81)	16.70 (317.90)	15.79 (333.60)
methyl *tert*-amyl ether	9.806 (303.37)	9.675 (317.90)	9.556 (332.60)
tetrahydrofuran	2.343 (303.10)	2.297 (317.90)	2.240 (333.60)
1,4-dioxane		1.478 (317.90)	1.276 (332.70)
furan		2.430 (317.90)	
pyridine		1.174 (317.90)	1.048 (332.70)
water[b]	3.097 (303.10)	2.673 (317.90)	2.260 (332.60)

[a] Calculation with saturation fugacity coefficient $\varphi_i^s = 1$. [b] After correction of the observed adsorption effects (Jönsson and Mathiasson, 1979).

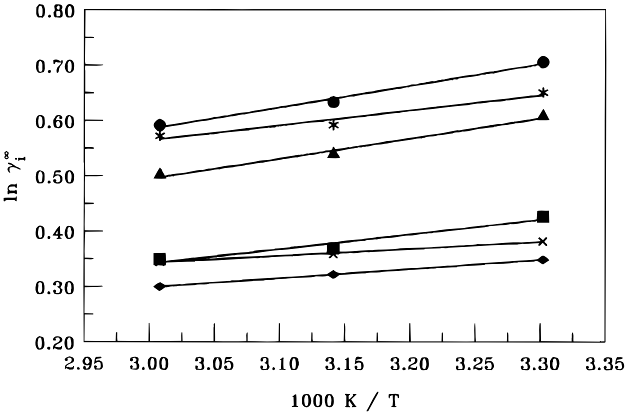

Figure 1. Activity coefficients at infinite dilution, γ_i^∞, for six different ethers in the selective solvent *N,N*-dibutylformamide as a function of temperature *T*: (●) isopropyl *tert*-butyl ether; (*) diisopropyl ether; (▲) ethyl *tert*-butyl ether; (■) methyl *tert*-amyl ether; (×) diethyl ether; (◆) methyl *tert*-butyl ether; (—) linear regression.

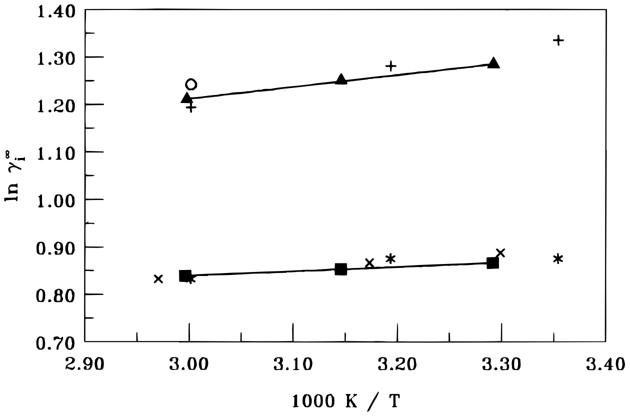

Figure 2. Activity coefficients at infinite dilution, γ_i^∞, for benzene and toluene in the selective solvent sulfolane as a function of temperature *T*: benzene in sulfolane (■) this work, (*) Rawat et al. (1976), (×) Gaile et al. (1974); toluene in sulfolane (▲) this work, (+) Rawat et al. (1976), (○) Schiller (1989); (—) linear regression of the present data.

of the limiting activity coefficients ($\bar{H}_i^{E,\infty} > 0$) is in good agreement with the data obtained from excess enthalpy measurements for both solutes (de Haan and Gmehling, 1996). Thus the results of the excess enthalpy measurements ($h^E > 0$, see Figure 4) support the former prediction. For all other systems included in this comparison (Möllmann, 1996) the temperature dependence found from gas chromatographic measurements is confirmed by data from

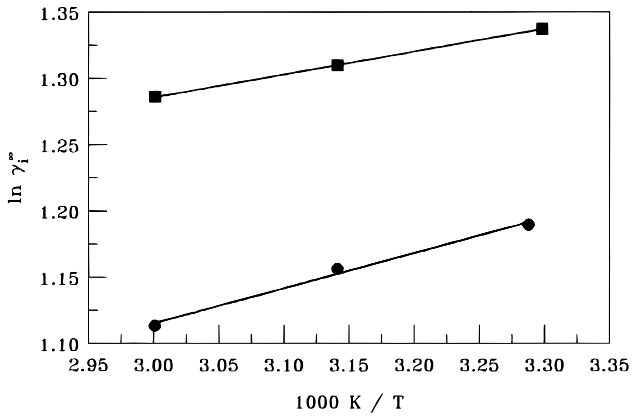

Figure 3. Activity coefficients at infinite dilution, γ_i^∞, for toluene (■) and propyl acetate (●) in the selective solvent *N*-methylacetamide as a function of temperature *T*. (—) Linear regression.

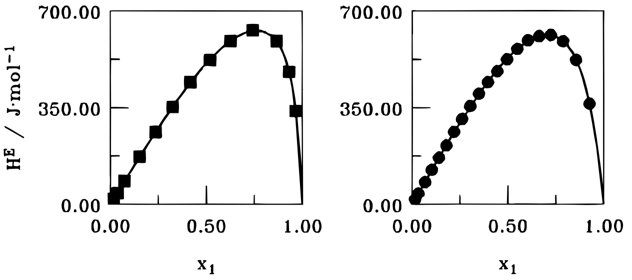

Figure 4. h^E data at 363.15 K for two mixtures containing *N*-methylacetamide: (■) toluene (1) + *N*-methylacetamide (2); (●) propyl acetate (1) + *N*-methylacetamide (2); (—) polynomial interpolation. Data taken from de Haan and Gmehling (1996).

various h^E measurements (Christensen et al., 1984). The absolute degree of exactness of the partial molar excess enthalpy at infinite dilution depends to a great extent on the quality of the experimentally determined activity coefficients at infinite dilution. It is evident that, in particular for systems where the slope of the straight line (ln γ_i^∞ vs 1000/T) is sufficiently large, a satisfactory to good reproduction of the value for the partial molar excess enthalpy at infinite dilution is possible in spite of the GLC experimental error of on average 3%. A criterion for the reliability of the data determined by gas–liquid chromatography can, however, already be seen in the correct reproduction of the direction of the temperature dependence of the limiting activity coefficients, which can be recognized from the sign of the partial molar excess enthalpy.

Conclusion

Gas–liquid chromatography is an ideal technique for the measurement of activity coefficients at infinite dilution, especially when the vapor pressure of the stationary phase is low. This situation is present in many distillation processes commonly encounterd in chemical industry where a high boiling solvent is added near the top of the column in order to separate a binary mixture (close-boiling or azeotropic) by means of extractive distillation. In this article systematic measurements of γ^∞ in four suitable selective solvents have been presented. By application of thermodynamic principles (i.e. the Gibbs–Helmholtz equation) the reliability of the data measured by gas–liquid chromatography can easily be checked using excess enthalpy data. The γ^∞ data can be used for the synthesis and design of separation processes, e.g. to determine and compare the selective effect caused by the addition of different solvents to a given binary mixture. Another important purpose of our investigations is the further development of thermodynamic models, such as modified UNIFAC (Weidlich and Gmehling, 1987; Gmehling et al., 1993) for the prediction of phase equilibrium data.

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Glossary

α_{ij}	separation factor of components i and j
$(\alpha_{ij})_k^\infty$	separation factor at infinite dilution of components i and j in solvent k
γ_i	activity coefficient of component i
γ_i^∞	activity coefficient at infinite dilution of component i
φ_i^s	solute fugacity coefficient of component i in the saturated state
H^E	molar excess enthalpy (J/mol)
$\bar{H}_i^{E,\infty}$	partial molar excess enthalpy at infinite dilution of component i (J/mol)
M_L	molar mass of solvent (g/mol)
P_i^s	saturation pressure of component i (kPa)
R	gas constant (J/(mol K))
V_g^0	specific net retention volume corrected to 0 °C (m^3/kg)
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i

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