

Measurement of Activity Coefficients at Infinite Dilution Using Gas–Liquid Chromatography. 7. Results for Various Solutes with *N*-Methyl-2-piperidone as Stationary Phase

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Activity coefficients at infinite dilution provide a useful tool for the selection of solvents for extractive distillation or extraction. In this work activity coefficients at infinite dilution are reported for 36 solutes (alkanes, alkenes, alcohols, ketones, aromatic hydrocarbons, cyclic hydrocarbons, aldehydes, ethers, esters, halocarbons, and acetonitrile) in *N*-methyl-2-piperidone at three temperatures (303.41, 313.43, and 323.45) K, measured with the help of gas–liquid chromatography. The experimental data are compared with data from literature and with the results of the modified UNIFAC (Dortmund) method. Furthermore the selectivity of *N*-methyl-2-piperidone for the separation of hexane from benzene was compared with the selectivity of *N*-methyl-2-pyrrolidone and *N*-methyl-6-caprolactam. The observed temperature dependence of the activity coefficients at infinite dilution is confirmed using excess enthalpy data predicted with modified UNIFAC (Dortmund).

Introduction

The separation of systems with separation factors equal to or near unity requires the use of additives that are also known as entrainers. In the case of extractive distillation, the entrainer is added in order to alter the ratio of the activity coefficients of the substances to be separated. To be able to estimate the selectivity of an entrainer, it is often sufficient to know the separation factor at infinite dilution of component *i* and *j* in the solvent *k* (Gmehling and Brehm, 1996)

$$(\alpha_{ij})_k^\infty = \frac{\gamma_i^\infty P_i^s}{\gamma_j^\infty P_j^s} \quad (1)$$

N-methyl-2-pyrrolidone (NMP) and *N*-methyl-6-caprolactam (NMC) are standard selective solvents used in commercial aliphatic/aromatic separation processes. *N*-methyl-2-pyrrolidone has a 5-ring structure, while *N*-methyl-6-caprolactam has a 7-ring structure (see Figure 1). One of the objectives of the experiments was to investigate the effect of the ring size on the separation factor of both compounds by measuring the activity coefficients at infinite dilution of various solutes in the 6-ring derivative *N*-methyl-2-piperidone (NMPI). Therefore, activity coefficients at infinite dilution have been measured for 36 solutes (alkanes, alkenes, alcohols, ketones, aromatic hydrocarbons, cyclic hydrocarbons, aldehydes, ethers, esters, halocarbons, and acetonitrile) in the solvent *N*-methyl-2-piperidone at the temperatures (303.41, 313.43, and 323.45) K.

The presence of adsorption effects were examined by varying the solvent liquid loading. No adsorption at the liquid or at the solid interface was observed contrary to

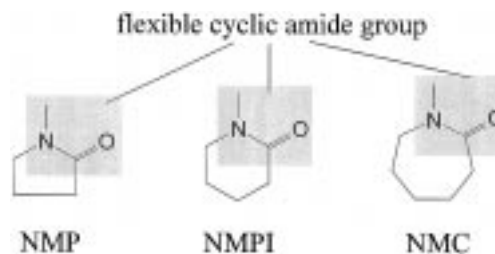


Figure 1. Molecular structures of *N*-methyl-2-pyrrolidone (NMP), *N*-methyl-2-piperidone (NMPI), and *N*-methyl-6-caprolactam (NMC).

the observations in our previous investigations using 1-octanol as solvent (Gruber et al., 1997).

Group contribution methods for estimating activity coefficients play an important role in solving various problems in both the chemical and petrochemical industries. The modified UNIFAC (Dortmund) model (Gmehling et al., 1993) provides great improvements over the original UNIFAC method and over other group contribution methods. It does not only afford reliable results for γ^∞ but also comparable predictions for vapor–liquid equilibria (VLE), excess enthalpies (H^E), and solid–liquid equilibria (SLE). Therefore and since the other UNIFAC versions cannot be applied because of missing groups, the experimental results were compared with the predicted results of the modified UNIFAC (Dortmund) method. With the help of the flexible cyclic amide group (cy-CONC, see Figure 1) good results are attained for modified UNIFAC (Dortmund).

Different techniques (Gmehling et al., 1994) can be applied for the measurement of γ^∞ values of organic substances in various solvents, e.g., static methods, dilutor technique, and gas–liquid chromatography (GLC), Reliable γ^∞ values are obtained from measurements with a static apparatus (isothermal *P*–*x* data). However the measurement of γ^∞ with the static method is very time-consuming. The measurement using headspace gas chro-

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matography (also a static method resulting in isothermal x - y data) for systems with similar boiling components cause great analytical problems and require considerable calibration efforts when—as in our case—the components show great vapor pressure differences. Another method is the dilutor technique. This method is based on the analysis of the variation of the vapor-phase composition obtained by stripping a highly diluted liquid mixture with an inert gas maintained at a constant flow. In comparison to GLC, the dilutor technique is much more time-consuming. Therefore gas-liquid chromatography was chosen as the most preferable measuring technique for the planned investigations. This technique requires the careful preparation of the column and allows the measurement of a great number of γ^∞ values in a rather short time. The reliability of the γ^∞ obtained by GLC has already been demonstrated by different authors (Gmehling et al., 1994).

Experimental and Measurement Procedure

The solid support used as the stationary phase for all measurements was Chromosorb W-AW-DMCS 60-80 mesh (acid-washed dimethyldichlorosilane-treated chromosorb). The support used was chosen due to the reduction of adsorption on silanized supports. The carrier material was coated with the solvent with methanol as a solubilizer in a rotary evaporator. After the solubilizer was removed, the column (length 200 mm, inner diameter 4.1 mm) was carefully filled with the coated solid support. The liquid loading (i.e., the amount of stationary phase or solvent on the inert carrier material) was determined gravimetrically. The gas chromatograph used for these investigations was developed in our laboratory. A detailed scheme of the gas chromatograph and the description of the measurement procedure is given by Knoop et al. (1989). The solvent used was *N*-methyl-2-piperidone with a purity greater than 99.8% (GLC analysis of peak areas, CP-Wax 52 column, temperature 150 °C, FID detector). Results for 36 solutes (alkanes, alkenes, alcohols, ketones, aromatic hydrocarbons, cyclic hydrocarbons, aldehydes, ethers, esters, halocarbons, and acetonitrile) in the solvent *N*-methyl-2-piperidone were obtained at the temperatures (303.41, 313.43, and 323.45) K. Since GLC is itself a separation technique, the results are not influenced by small solute impurities. Therefore commercially available solutes were used for the investigations without further purification.

To determine if solvent losses occurred during the course of the experiment, the coated solid support is removed from the column and placed into porcelain crucibles in samples of 0.3 g. The solvent is then evaporated from the solid support for several hours in a muffle furnace at 500 °C. 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. With the use of presaturators the loss of solvent was kept to a minimum. This ranged typically between 2 and 4 mass % over a period of about 6 h and was taken into account assuming linear solvent loss during the isothermal measurements.

Surface effects are very common in GLC systems and have to be considered in any proposed investigation of solution behavior. The use of acid-washed Chromosorb W treated with dimethyldichlorosilane as well as the relatively high amount of solvent on the packing kept adsorption on the solid support to a minimum.

The determination of γ^∞ requires the following information: the net retention time of the solute (t_N), the temperature (T), column inlet and outlet pressures (P_i and P_o),

the carrier gas flow rate, and the amount of the stationary phase on the solid support. From these experimentally determined parameters, the specific retention volume (V_g^0) corrected to 0 °C is determined. The activity coefficient at infinite dilution is then given by

$$\gamma_i^\infty = \frac{RTm_L}{V_g^0 P_i^s M_L \varphi_i^s} \quad (2)$$

where R is the gas constant, T the absolute experimental temperature, m_L the mass of the solvent, M_L the molar mass of the solvent, and P_i^s the saturation vapor pressure of the solute. P_i^s is calculated using 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 following Gmehling and Kolbe (1992). The required critical data and acentric factors are also taken from the DDB. The net retention time is equal to the difference between the retention time, t_R , of the solute (solute peak) and the dead time, t_A , (peak caused by air that 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 a result of phase equilibrium behavior.

Results and Discussion

Activity coefficients at infinite dilution of various types of solutes were determined on *N*-methyl-2-piperidone at three temperatures and two different solvent column loadings (12.0 and 16.8 mass %). No adsorption effects were observed. The choice of the solutes studied was determined in part by the temperature range covered; thus, some high-boiling compounds could not be measured at low temperatures because of very long retention times.

The specific retention volume V_g^0 (corrected to 0 °C) was calculated for all the solutes at different solvent liquid loadings (V_L) and different temperatures. Then from eq 2 the activity coefficients at infinite dilutions are determined. The results are listed in Table 1. Apart from the actual values obtained, these measurements also contain information regarding the temperature dependence of the boundary activity coefficients of the various solutes in *N*-methyl-2-piperidone. The γ^∞ values are not directly measured; rather, they are calculated from other measured parameters (eq 2). The main source of error in the calculation of γ^∞ is the measurement of the mass of the stationary phase in the column. This error was assumed to be approximately 2%. In addition, there is a small error in the determination of the retention time (Knoop et al., 1989). This is dependent on the time difference between t_R and t_A and decreases with increasing net retention time. To reduce this error, appropriate gas-chromatographic conditions were used. The net retention times were between 0.120 and 28.3 min. The total error in determining V_N is about

$$S_{V_N} = 2.5\%$$

The resulting error in the γ^∞ , taking into account that the Antoine constants taken from the DDB and used in the calculation of the saturation vapor pressure are also subject to an error, is

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

Table 1. Experimental Activity Coefficients at Infinite Dilution, γ_i^∞ , for Various Solutes in the Solvent *N*-Methyl-2-piperidone as a Function of Temperature

solute	γ_i^∞		
	$T=303.41$ K	$T=313.43$ K	$T=323.45$ K
pentane	7.98	7.37	6.75
hexane	9.51	8.45	7.95
heptane	10.72	9.70	8.88
octane	12.49	11.13	10.25
2-methylbutane	7.84	7.37	6.98
2-methylpentane	9.58	8.45	7.84
methanol	0.39	0.39	0.41
ethanol	0.49	0.50	0.51
benzene	0.91	0.92	0.94
toluene	1.21	1.22	1.26
1-pentene	4.28	4.15	4.03
1-hexene	4.93	4.71	4.54
cyclohexane	5.45	5.07	4.80
methylcyclohexane	6.34	5.87	5.56
cyclohexene	3.21	3.08	2.98
cyclopentane	4.42	4.18	3.99
methylcyclopentane	5.57	5.23	4.99
oxolane	1.34	1.33	1.31
diethyl ether	2.85	2.83	2.81
diisopropyl ether	4.32	4.26	4.10
methyl <i>tert</i> -butyl ether	2.85	2.81	2.77
ethyl <i>tert</i> -butyl ether	3.88	3.81	3.67
methyl <i>tert</i> -amyl ether	3.18	3.13	3.10
isopropyl <i>tert</i> -butyl ether ^a	4.69	4.56	4.38
acetone	1.18	1.21	1.22
2-butanone	1.22	1.25	1.25
2-pentanone	1.33	1.36	1.36
4-methyl-2-pentanone	1.50	1.51	1.48
acetonitrile	0.74	0.79	0.81
acetaldehyde	1.06	1.08	1.09
isobutyraldehyde	1.30	1.33	1.34
methyl acetate	1.44	1.47	1.49
ethyl acetate	1.56	1.58	1.59
propyl acetate	1.70	1.72	1.72
dichloromethane	0.22	0.26	0.28
chloroform	0.12	0.14	0.15

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

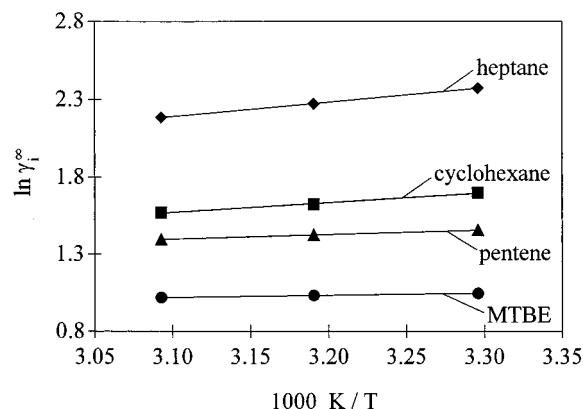
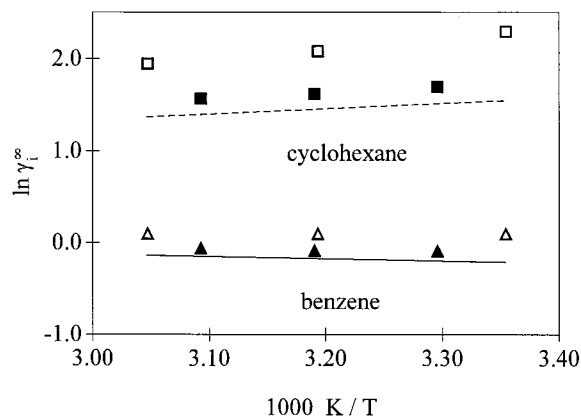
**Figure 2.** Experimental activity coefficients at infinite dilution γ_i^∞ , for four solutes in the solvent *N*-methyl-2-piperidone (NMPI) as a function of temperature: (◆) heptane; (■) cyclohexane; (●) MTBE; (▲) 1-pentene; (—) linear regression.

Figure 2 shows examples of the linear relationship between the natural logarithm of the activity coefficients and the inverse absolute temperature for selected solutes (heptane, cyclohexane, pentene, and MTBE) in *N*-methyl-2-piperidone. In Figure 3 the experimental data for the solutes benzene and cyclohexane are compared with values taken from the literature and with predicted γ_i^∞ values using modified UNIFAC (Do) (Gmehling et al., 1993). The graph shows that the predicted values are in accordance

**Figure 3.** Activity coefficients at infinite dilution γ_i^∞ , for two solutes in the solvent *N*-methyl-2-piperidone (NMPI) as a function of temperature: this work, (■) cyclohexane, (▲) benzene; published values, (□) cyclohexane, (△) benzene, Muller et al. (1976); predicted values using modified UNIFAC (Do) (Gmehling et al., 1993), (---) cyclohexane, (—) benzene.

with the new experimental data. However, the values taken from the literature (no gas-phase imperfections were considered) are usually higher than the data presented.

The temperature dependence of the γ_i^∞ values is important to judge the temperature dependence of the selectivity at infinite dilution. A graph of $\ln \gamma_i^\infty$ versus the inverse absolute temperature often shows a straight line in a limited temperature interval (see Figures 2 and 3). According to the Gibbs–Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution $H_i^{E,\infty}$ can directly be obtained from the slope of this straight line (Gmehling and Kolbe, 1992).

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right)_{P,x} = \frac{H_i^{E,\infty}}{R} \quad (5)$$

For most of the solutes measured, the limiting activity coefficients tend toward ideal behavior ($\gamma_i^\infty = 1$) when the temperature increases (alkanes, alcohols, benzene, alkenes, cycloalkanes, ethers, and halocarbons). The temperature dependence found by gas chromatography can be confirmed by H^E data. Since there are no experimental H^E data, the observed temperature dependence is compared with predicted H^E data using modified UNIFAC (Do). For all systems where interaction parameters are available (NMPI + alkanes, alkenes, aromatics, cycloalkanes, and cycloalkenes) the temperature dependence is in accordance with the predicted data. Furthermore, for the polar compounds a less pronounced temperature dependence is observed (smaller H^E values) than for the different hydrocarbons.

Table 2 compares the separation factors of different alkane/aromatic systems at infinite dilution of *N*-methyl-2-piperidone with the values for NMP and NMC. From the table it can be seen that NMP shows the highest selectivity for the separation of aromatic from aliphatic compounds. The separation factor $(\alpha_{12})_k^\infty$ decreases with the number of carbon atoms in the ring system. The separation factors at infinite dilution $(\alpha_{12})_k^\infty$ increase from NMC to NMP for all systems.

Figure 4 shows the influence of the solvent (NMP, NMPI, and NMC) on the γ_i^∞ values for the selected solutes octane and cyclohexene. It can be seen that γ_i^∞ increases with decreasing number of carbon atoms in the ring structure of the solvents. The same effect is also observed for other investigated solutes.

Table 2. Experimental Separation Factors at Infinite Dilution ($\alpha_{12}^{\infty}_k$) for Various Alkane/Aromatic Systems for the Solvents *N*-Methyl-2-pyrrolidone (NMP), *N*-Methyl-2-piperidone (NMPI), and *N*-Methyl-6-caprolactam (NMC)

system	$(\alpha_{12}^{\infty}_k (t^{\circ}\text{C}))$		
	NMP ^a	NMPI ^b	NMC ^{c-f}
cyclohexane (1) + benzene (2)	6.45 (50.2)	5.11 (50.3)	3.99 (50.0)
methylcyclohexane (1) + toluene (2)	8.75 (50.2)	6.63 (50.3)	5.25 (60.0)
hexane (1) + benzene (2)	15.91 (50.2)	12.95 (50.3)	6.90 (50.0)
heptane (1) + toluene (2)	15.15 (50.2)	11.06 (50.3)	8.27 (55.0)

^aWeidlich et al. (1987). ^bThis work. ^cFrost and Bittrich (1974). ^dHradetzky et al. (1989). ^eSarius and Bittrich (1983). ^fWobst (1989).

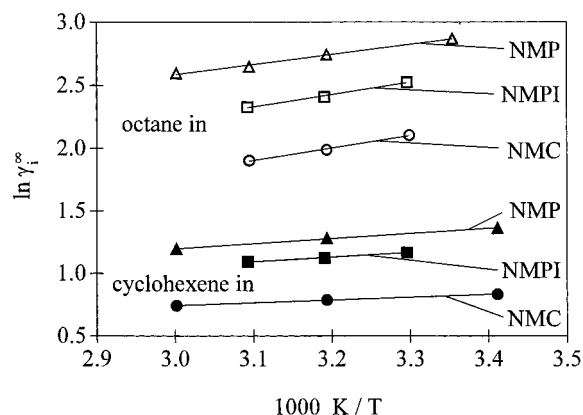


Figure 4. Activity coefficients at infinite dilution γ_i^{∞} , in the solvents *N*-methyl-2-pyrrolidone (NMP), *N*-methyl-2-piperidone (NMPI), and *N*-methyl-6-caprolactam (NMC) as a function of temperature: 1-octane in (\blacktriangle) NMP, Popescu et al. (1967); (\square) NMPI, this work; (\circ) NMC, Wobst (1989); (—) linear regression; cyclohexene in (\blacktriangle) NMP, Hradetzky et al. (1990); (\blacksquare) NMPI, this work; (\bullet) NMC, Vopel (1989); (—) linear regression.

Conclusion

Activity coefficients at infinite dilution for 36 solutes in *N*-methyl-2-piperidone have been measured at three different temperatures by GLC. This technique allows a fast and reliable determination of γ^{∞} . No adsorption effects were observed. The selectivity of the entrainer *N*-methyl-2-piperidone is compared with the selectivity of the widely used selective solvents NMP and NMC. Furthermore, the

activity coefficients at infinite dilution are compared with published and predicted values using modified UNIFAC (Do).

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