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Measurement of Activity Coefficients at Infinite Dilution Using Gas−Liquid Chromatography. 11. Results for Various Solutes with the Stationary Phases ϵ-Caprolactone and Ethyl Benzoate

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Using gas−liquid chromatography (GLC), activity coefficients at infinite dilution have been measured for 37 solutes (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, ethers, aldehydes, esters, and halocarbons) in the solvents ϵ-caprolactone and ethyl benzoate. The measurements were carried out in the temperature range between (303.15 and 343.15) K. The γ^∞ values obtained were compared with published data, and the observed temperature dependence of the limiting activity coefficients was confirmed using excess enthalpy data.

Introduction

Limiting activity coefficients have important practical applications for different industrial problems; for example, activity coefficients at infinite dilution can directly be used for the selection of selective solvents for extractive distillation or extraction processes. A typical application of extractive distillation or liquid−liquid extraction is the separation of aromatics from aliphatics.

In a systematic study the limiting activity coefficients have been determined for 37 substances in two solvents in order to obtain quantitative information for entrainer selection. The investigated solvents were chosen because no γ^∞ data are available in the literature and in the case of ϵ-caprolactone similar structured components are used as selective solvents in commercial extraction processes. The obtained γ^∞ values for the solvent ethyl benzoate were used in addition to VLE and H^E data to introduce a new aromatic ester group into the group contribution method mod. UNIFAC (Do) (Nienhaus, 2000). The GLC technique was chosen as the most preferable measuring technique for the planned investigations, because GLC shows several advantages in comparison to other methods, for example, static methods or the dilutor technique (Gruber et al., 1998; Kojima et al., 1997). After the careful preparation of the column, the GLC method allows the reliable measurement of γ^∞ values in a rather short time. The reliability of the γ^∞ data obtained by GLC has been confirmed by different authors (Gmehling et al., 1994).

Experimental Procedure

For all measurements Chromosorb P-AW-DMCS 60/80 mesh (acid-washed dimethyldichlorosilane-treated Chromosorb) was used as the solid support for the stationary phase. The coating of the predried carrier material with solvent was carried out with methanol (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. A scheme of the homemade gas chromatograph used for these investigations, the detailed description of the measurement procedure, and the most important equations for evaluation purposes together with the theoretical explanations are given by Knoop et al. (1989).

The solvents used, ϵ-caprolactone and ethyl benzoate, were applied with a purity > 99.8 mass % (GLC analysis of peak areas, CP-Wax 52 column, temperature 150 °C, FID detector) and a water content < 100 ppm (Karl Fischer titration). γ^∞ values for 37 solutes (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, alcohols, ketones, ethers, aldehydes, acetates, and halocarbons) were measured in the temperature range between 303.15 and 343.15 K. Since GLC itself is a separation technique, the results are not influenced by small solute impurities, and therefore, the solutes were used without further purification.

To check if solvent losses occurred during the measurements, the liquid loading was determined before and after the measurement gravimetrically. Under the stated conditions the pure uncoated Chromosorb suffers from a loss of mass due to the removal of strongly adsorbed water, which has been taken into account, too. With the use of presaturators, the loss of solvent was kept to a minimum. The maximum solvent loss was about 3 mass % over a period of about 8 h and was taken into account assuming linear solvent loss during the isothermal measurements. Furthermore, the experimental conditions (gas flow, solvent loss, etc.) were checked by measuring the net retention time of a reference substance (hexane) at regular intervals.

Equation 1 relates the activity coefficient of the solute at infinite dilution to the measured specific net retention volume (V_g°) at 0 °C:

$$\gamma_i^\infty = \frac{273.15R}{V_g^\circ P_i^s \varphi_i^s M_L} \tag{1}$$

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 calculated using Antoine constants taken from the Dortmund Data Bank (DDB). The saturation fugacity coefficient of the solute φ_i^s is calculated with the help of the Soave−Redlich−Kwong equation of state following

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Table 1. Experimental Activity Coefficients at Infinite Dilution (γ^∞) for Various Solutes in the Solvent Ethyl Benzoate

	γ^∞			
solute	313.15 K	323.15 K	333.15 K	343.15 K
pentane	2.77	2.72	2.65	2.61
hexane	2.99	2.89	2.81	2.73
heptane	3.16	3.05	2.95	2.86
octane	3.38	3.23	3.08	2.96
2-methylpentane	3.00	2.91	2.85	2.80
1-pentene	1.95	1.92	1.90	1.88
1-hexene	2.08	2.05	2.02	1.99
1-octene	2.32	2.26	2.22	2.18
cyclopentane	1.89	1.86	1.82	1.79
cyclohexane	2.21	2.14	2.08	2.01
methylcyclopentane	2.21	2.15	2.11	2.07
methylcyclohexane	2.36	2.28	2.21	2.14
cyclohexene	1.54	1.52	1.50	1.48
benzene	0.955	0.959	0.963	0.967
toluene	1.04	1.04	1.03	1.03
ethylbenzene	1.10	1.08	1.07	1.06
1,2-xylene	1.07	1.08	1.09	1.10
1,3-xylene	1.08	1.10	1.11	1.12
1,4-xylene	1.10	1.11	1.12	1.13
diethyl ether	1.29	1.30	1.30	1.31
diisopropyl ether	1.72	1.74	1.73	1.76
methyl *tert*-butyl ether	1.34	1.35	1.36	1.37
ethyl *tert*-butyl ether	1.56	1.57	1.57	1.58
methyl *tert*-amyl ether	1.38	1.40	1.41	1.42
isopropyl *tert*-butyl ether	1.79	1.76	1.74	1.72

Gmehling and Kolbe (1992). The required critical data and acentric factors are also taken from the DDB.

According to Conder and Young (1978), sometimes adsorption effects have to be taken into account. For example, adsorption at the gas−liquid interface occurs with increasing polarity of the solvent. Polar solutes on nonpolar stationary phases lead to adsorption at the gas−liquid interface, often accompanied by adsorption on the solid support.

To examine the presence of adsorption effects, the relative amount of stationary phase (liquid loading: 15−25%) and the sample volume of the injected solutes (0.02−0.5 μL) were varied. Contrary to the observations in our previous investigations for *n*-octanol as stationary phase (Gruber et al., 1997), no adsorption effects were observed.

Results and Discussion

The values of the activity coefficients at infinite dilution for the investigated solutes in the solvents ϵ-caprolactone and ethyl benzoate at different temperatures are listed in Tables 1 and 2. The main source of error in the calculation of the specific retention volume corrected to 0 °C (V_g°) is the measurement of the mass of the stationary phase in the column (±2%). In addition, there is a small error in the determination of the difference between the retention time and the dead time (Knoop et al., 1989). The total error in the determination of the specific retention volume is about ±2.5%. Taking into account that the Antoine constants taken from the DDB used for the calculation of the saturation vapor pressure are also subject to error, the resulting error in γ^∞ is ±3.0%. Measurements with different amounts of stationary phase or with different flow rates lead to results within this error.

Limiting activity coefficients were measured for several classes of compounds. Figure 1 shows the linear relationship between the natural logarithm of the limiting activity coefficient and the inverse absolute temperature for four different alkanes in ϵ-caprolactone. The γ^∞ values for the alkanes range from a minimum of 9.02 for pentane at 333.15 K to a maximum of 19.9 for octane at 303.15 K. As expected, the limiting activity coefficient diminishes with decreasing chain length (octane > heptane > hexane > pentane). On the other hand, the γ^∞ for benzene in ethyl benzoate ranges from 0.955 at 313.15 K to 0.967 at 343.15 K, which is an indication of the similar chemical nature of benzene and ethyl benzoate.

Table 2. Experimental Activity Coefficients at Infinite Dilution (γ^∞) for Various Solutes in the Solvent ϵ-Caprolactone

	γ^∞		
solute	303.15 K	318.15 K	333.15 K
pentane	10.3	9.74	9.02
hexane	12.9	11.9	10.8
heptane	16.0	14.5	13.0
octane	19.9	17.7	15.7
1-pentene	5.85	5.62	5.36
1-hexene	7.24	6.85	6.45
1-octene	11.1	10.2	9.32
cyclohexane	7.87	7.38	6.74
cyclohexene	4.53	4.34	4.13
benzene	1.39	1.39	1.41
toluene	1.83	1.82	1.82
methanol	1.65	1.56	1.44
ethanol	2.00	1.84	1.66
1-propanol	2.10	1.89	1.67
2-propanol	2.18	1.99	1.83
diethyl ether	3.09	3.06	3.01
diisopropyl ether	5.31	5.21	5.07
methyl *tert*-butyl ether	3.25	3.23	3.18
ethyl *tert*-butyl ether	4.86	4.75	4.65
methyl *tert*-amyl ether	4.00	3.92	3.86
tetrahydrofuran	1.42	1.41	1.40
acetone	1.25	1.24	1.23
2-butanone	1.37	1.35	1.34
2-pentanone	1.57	1.56	1.55
acetaldehyde	1.19	1.17	1.15
vinyl acetate	1.63	1.61	1.59
dichloromethane	0.529	0.560	0.591
chloroform	0.404	0.448	0.496

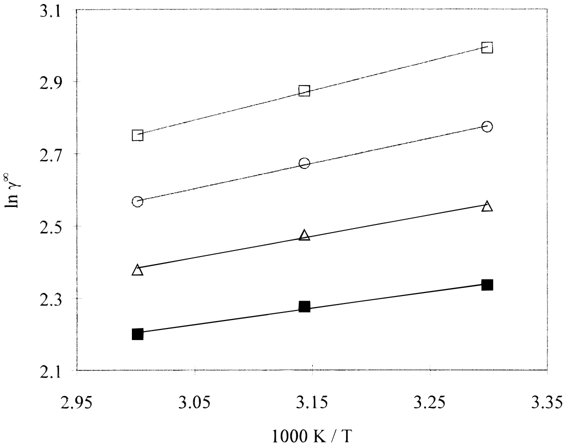

Figure 1. Experimental activity coefficients at infinite dilution γ^∞ for four solutes in the solvent ϵ-caprolactone as a function of temperature: □, octane; ○, heptane; △, hexane; ■, pentane; —, linear regression.

A graph of ln γ^∞ versus the inverse absolute temperature often shows a straight line in a limited temperature range (see Figure 1). According to the Gibbs−Helmholtz equation

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial 1/T}\right)_{P,x} = \frac{H_i^{\mathrm{E},\infty}}{R} \tag{2}$$

the value for the partial molar excess enthalpy at infinite dilution ($H_i^{\mathrm{E},\infty}$) can directly be obtained from the slope of

Table 3. Calculated Partial Molar Excess Enthalpies at Infinite Dilution ($H_i^{E,\infty}$) for Solute (2) in Ethyl Benzoate

solute (2)	$\bar{H}_2^{E,\infty\ a}$ (J/mol)	$\bar{H}_2^{E,\infty\ b}$ (J/mol)	ref
pentane	1838	3468	Ortega et al. (1995)
hexane	2700	2725	Grolier et al. (1974)
heptane	3008	3570	Grolier et al. (1974)
octane	4027	4380	Grolier et al. (1974)
benzene	−39	−94	Grolier et al. (1974)
ethylbenzene	985	178	Grolier et al. (1974)

[a] Calculated by linear regression from experimental γ^∞ data ($\vartheta = 40-70$ °C). [b] Calculated from H^E data ($\vartheta = 25$ °C).

this straight line (Gmehling and Kolbe, 1992). This means that experimental H^E data can be used to confirm the observed experimental temperature dependence. With the help of a polynomial (Redlich−Kister or SSF (sum of symmetrical functions)), the value of the partial molar excess enthalpy at infinite dilution ($H_i^{E,\infty}$) can be calculated. In Table 3 the partial molar excess enthalpies at infinite dilution ($H_i^{E,\infty}$) calculated by linear regression for different solutes in the solvent ethyl benzoate are compared with values calculated from H^E data. In all cases the $H_i^{E,\infty}$ values obtained by GLC agree reasonably well with the values derived from experimental H^E data. The increase of the γ^∞ values for benzene with an increase in temperature results in negative values for the partial molar excess enthalpies at infinite dilution. The correct reproduction of the temperature dependence of the limiting activity coefficients is a suitable criterion for the reliability of γ^∞ data.

Conclusion

Activity coefficients at infinite dilution for 37 solutes in the solvents ϵ-caprolactone and ethyl benzoate have been measured at different temperatures with the help of GLC. The GLC technique was chosen due to the possibility of a fast and reliable determination of γ^∞ values. The reliability of the obtained data was confirmed by verifying the temperature dependence of the limiting activity coefficients using experimental H^E data. The data can be used for fitting g^E model as well as group interaction parameters required for the synthesis and design of chemical processes.

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