Measurement of Activity Coefficients at Infinite Dilution Using Gas−Liquid Chromatography. 6. Results for Systems Exhibiting Gas−Liquid Interface Adsorption with 1-Octanol

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Activity coefficients at infinite dilution provide a useful tool for solvent selection in extractive distillation or extraction processes. In this work activity coefficients at infinite dilution for various solutes (alkanes, cycloalkanes, alcohols, aromatic hydrocarbons, xylenes and alkenes) in the solvent 1-octanol were measured at four temperatures, (293.44, 303.45, 313.55, and 323.43) K, with the help of gas−liquid chromatography. The adsorption at the gas−liquid interface between the solutes and the solvent was examined by varying the solvent liquid loading in the columns. Corrected retention values taking adsorption effects into account are determined and are used to calculate the activity coefficients at infinite dilution. These values compare well with various activity coefficients taken from the literature using different techniques and the predicted values using the modified UNIFAC (Dortmund) method. An important application of the present data can be seen in the use of 1-octanol as a solvent for processes such as extractive distillation or extraction. It is sufficient to know the separation factor at infinite dilution of the components to be separated in order to determine the applicability of 1-octanol as a selective solvent.

Introduction

Activity coefficients at infinite dilution (γ^∞) are of interest not only to the practicing chemist and chemical engineer but also from a theoretical point of view. γ^∞ describes the behavior of a dissolved compound (the solute) that is completely surrounded by solvent molecules. Values of limiting activity coefficients have important, practical, and direct applications for industrial problems, since activity coefficients at infinite dilution can directly be used for the selection of selective solvents for extractive distillation or extraction. With the aid of activity coefficients at infinite dilution as a function of temperature, the occurrence of azeotropic data can be predicted. Therefore the reliable knowledge of these data is particularly important for the synthesis of separation processes. Gmehling and Möllmann (1997) demonstrate how experimental azeotropic data (Gmehling et al., 1994) and activity coefficients at infinite dilution (Gmehling et al., 1994) can be applied for this purpose.

In distillation processes selective solvents are used when components cannot be separated in the case of azeotropic points. In many cases a knowledge of the relative volatility at infinite dilution (α_{ij}^∞) is a criterion for the selection of a solvent. In the limit of 100% solvent concentration, the relative volatility for components i and j is given by

$$\alpha_{ij}^\infty = \frac{\gamma_i^\infty}{\gamma_j^\infty}\frac{P_i^s}{P_j^s} = S_{ij}^\infty \frac{P_i^s}{P_j^s} \tag{1}$$

where P_i^s is the saturation vapor pressure.

The activity coefficients at infinite dilution can be measured by various techniques e.g. gas−liquid chromatography (GLC). GLC is a very rapid and reliable method. In a gas chromatographic column the liquid is effectively spread out over a very small depth. This implies a very large surface to volume ratio. If there is any tendency for the solute to adsorb preferentially at the gas−liquid interface (liquid surface), its effects will be highly magnified when the liquid is spread out on a chromatographic support. For this reason GLC is inherently well suited to investigate liquid surface adsorption. Martin (1961) concluded that adsorption at the liquid surface interface increases with an increase in solvent polarity. Therefore in the case of 1-octanol as solvent, surface effects have to be taken into account in order to calculate the activity coefficients from retention data.

Martin (1961) was able to demonstrate that the adsorption at the gas−liquid interface contributed to the retention volume when the solute is eluted from the column. Taking this into account, he formulated the following equation for the net retention volume

$$V_N = K_L V_L + K_I A_I \tag{2}$$

where K_L (dimensionless) and V_L are the bulk solution partition coefficient and the volume of liquid on the column, respectively, A_I is the area of the gas−liquid interface in the column, and K_I is the adsorption coefficient. The equation is valid only at infinite dilution.

The aim of the measurements carried out in this work is to determine the ability of 1-octanol to be used as a solvent for extractive distillation and extraction for the separation of specific mixtures, e.g. xylenes, alcohols, and aromatic hydrocarbons from cyclic hydrocarbons. The determination of the activity coefficients at infinite dilution of various solutes in 1-octanol can be used for the calculation of octanol/water partition coefficients (K_{OW}). This is due to the similarities of the activity coefficients at infinite

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dilution of solutes both in pure 1-octanol and in water-saturated 1-octanol (Dallas, 1995). Octanol/water partition coefficients together with Henry coefficients and water solubilities can serve as basic physiochemical quantities for estimating the effects on the environment that can arise from potentially hazardous substances (Wienke and Gmehling, 1997). A further aim was to investigate the effects of adsorption at the gas−liquid interface in the determination of the activity coefficients at infinite dilution. In a systematic study the activity coefficients at infinite dilution of 20 compounds have been determined experimentally in the temperature range 293.44 K to 323.43 K. In order to investigate adsorption effects the solvent column loading has been varied between 10 and 25%.

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 in adsorption on silanized supports. The carrier material was coated with the solvent with methanol as a solubilizer in a rotary evaporator. The solubilizer was removed and 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 apparatus used in these investigations was developed in our laboratory. A detailed scheme of the gas chromatograph and the description of the measurement procedure are given by Knoop et al. (1989). The solvent used was 1-octanol and had a purity higher than 99.8% (GLC analysis of peak areas, CP-Wax 52 column, temperature 150 °C, FID detector). Results for 20 solutes (alkanes, alkenes, cycloalkanes, aromatic hydrocarbons, alcohols, and xylenes) were obtained at 293.44, 303.45, 313.55, and 323.43 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.

In order to determine if any solvent was lost during the course of the experiment, the coated solid support was removed from the column and placed into porcelain crucibles in samples of 0.3 g. The solvent was 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 8 h.

Surface effects are very common in GLC systems and need 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. However the adsorption of the solute at the gas−liquid interface had to be taken into consideration due to the polar nature of the solvent (1-octanol) used. This is done by varying the loading of liquid solvent in the column. By rearranging eq 2, the following relation is obtained

$$V_g \propto \frac{V_N}{V_L} = K_L + \frac{K_I A_I}{V_L} \tag{3}$$

where V_g, the specific retention volume, is proportional to the ratio V_N/V_L (V_N, net retention volume; V_L, volume of the liquid phase). If V_g is independent of V_L over a wide range of V_L, no surface effects have to be taken into account.

The determination of γ^∞ requires the following information: the net retention time of the solute (t_N), the measuring absolute 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 (Gmehling et al., 1994). From these experimentally determined parameters, the net retention volume V_N is calculated in order to take into account the effects at the gas−liquid interface. The activity coefficient at infinite dilution is given by

$$\gamma_i^\infty = \frac{RTm_L}{V_N P_i^s M_L \varphi_i^s} \tag{4}$$

where R is the gas constant, T is the absolute temperature of the experiment, M_L is the molar mass of the solvent, m_L is the mass of the solvent, and P_i^s is 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 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 caused directly by the phase equilibrium behavior. However, in the case where gas−liquid adsorption takes place in the column, eq 4 is modified to

$$\gamma_i^\infty = \frac{RT\rho_L}{K_L P_i^s M_L \varphi_i^s} \tag{5}$$

where ρ_L is the density of the solvent and K_L the bulk solution partition coefficient. The best method of determining K_L in the presence of interfering adsorption effects is to plot V_N/V_L (or V_g) against $1/V_L$. Then according to eq 4 K_L is obtained from the intercept (Conder and Young, 1979). In this way the activity coefficients for 20 solutes in 1-octanol at 4 temperatures were determined.

Results and Discussion

The net retention volume (V_N) was calculated for all the solutes at different solvent liquid loading (V_L). In order to correct for gas−liquid adsorption, the graphs of V_N/V_L versus $1/V_L$ were drawn for each solute and the partition bulk coefficient (K_L) is obtained from the intercept. Two examples are given in Figure 1. The K_L value is then used in eq 5 to calculate the activity coefficient at infinite dilution for bulk solvent loading, i.e. assuming that no adsorption of the solute at the gas−liquid interface occurs. After gas−liquid adsorption was corrected for, the activity coefficient for all the solutes decreased by about 10%. The values for K_L and the corrected γ^∞ at the temperatures 293.44, 303.48, 313.55, and 323.43 K are given in Tables 1 and 2 respectively.

Apart from the actual values obtained, these measurements also afford information regarding the temperature dependence of the boundary activity coefficients of the various solutes in 1-octanol. The γ^∞ is not directly measured; rather, it is calculated from other measured parameters (eqs 4 and 5). Thus the error of γ^∞ must be obtained from the law of propagation of errors. The following

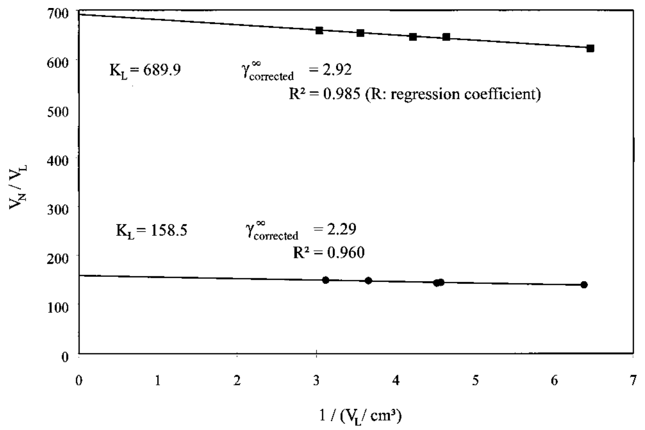

Figure 1. Determination of bulk solution partition coefficients, K_L, for 1-hexene (●) at 313.55 K and for heptane (■) at 303.45 K with linear regression (—).

Table 1. Experimental Bulk Solution Partition Coefficients, K_L, for Various Solutes in the Solvent 1-Octanol as a Function of Temperature Determined by Equation 3

	K_L			
solute	293.44 K	303.45 K	313.55 K	323.43 K
pentane	112.9	81.5	60.4	46.8
hexane	353.1	243.3	164.4	123.1
heptane	1115.3	689.9	450.5	323.7
octane	3584.2	2006.5	1227.9	845.8
benzene	793.8	510.3	360.6	265.2
toluene	2603.0	1588.4	1069.1	732.8
ethylbenzene	7064.2	4135.8	2591.4	1737.7
cyclohexane	683.3	448.7	324.3	231.8
methylcyclohexane	1386.5	877.1	608.1	428.7
cyclohexene	842.4	578.2	392.7	279.7
methanol	945.2	573.8	363.8	250.7
ethanol	2212.2	1250.5	746.3	494.8
1-propanol	7038.2	3636.9	2130.0	1286.0
2-propanol	3432.7	1841.1	1091.4	686.5
2-butanol	9646.3	4788.7	2763.6	1650.2
o-xylene	*a*	6344.3	3881.1	2418.0
m-xylene	*a*	4938.4	3206.1	2001.0
p-xylene	*a*	4784.7	3015.0	1933.5
1-pentene	98.9	71.1	54.9	42.7
1-hexene	318.5	214.5	158.5	116.9

[a] Due to the large retention times of the xylenes at 293.44 K, the partition coefficients could not be measured.

measured parameters can exhibit errors and must be taken into account in the error calculations with their corresponding standard deviations: the difference between the measured retention time and the dead time ($t_R - t_A$), 0.02 min; volume flow of carrier gas, 0.1 cm^3/min; mass of stationary phase (relative), 2%; pressure at column entrance, 0.001 bar; pressure at column exit, 0.003 bar; absolute temperature at the flow meter (T_{fm}), 0.2 K; absolute temperature of the water bath, 0.2 K. The error in the determination of the volume flow of the carrier gas, the pressure at the inlet and outlet, and the temperature at the flow meter are negligible. The main source of error in the calculation of the net retention volume is the measurement of the weight 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. This is dependent on the time difference between t_R and t_A and decreases with increasing net retention time. In order to reduce this error appropriate gas-chromatographic conditions were used. The total error in determining V_N is about

$$S_{V_N} = 2.5\% \qquad (6)$$

Table 2. Experimental Activity Coefficients at Infinite Dilution, γ^{∞}, for Various Solutes in the Solvent 1-Octanol as a Function of Temperature Determined by Equation 5

	$\gamma^{\infty\ a}$			
solute	293.44 K	303.45 K	313.55 K	323.43 K
pentane	2.46	2.42	2.39	2.32
hexane	2.70	2.62	2.66	2.53
heptane	2.90	2.92	2.89	2.71
octane	3.05	3.17	3.14	2.90
benzene	1.93	1.94	1.83	1.73
toluene	2.02	2.02	1.90	1.83
ethylbenzene	2.28	2.24	2.15	2.02
cyclohexane	2.18	2.17	2.02	1.98
methylcyclohexane	2.29	2.29	2.16	2.10
cyclohexene	1.94	1.94	1.82	1.78
methanol	1.25	1.25	1.25	1.19
ethanol	1.18	1.20	1.20	1.13
1-propanol	1.11	1.14	1.08	1.06
2-propanol	1.05	1.08	1.05	1.02
2-butanol	0.92	0.96	0.92	0.90
o-xylene	*b*	2.08	2.01	2.00
m-xylene	*b*	2.15	1.97	1.98
p-xylene	*b*	2.11	2.00	1.96
1-pentene	2.25	2.26	2.16	2.12
1-hexene	2.43	2.43	2.29	2.23

[a] The uncertainty in γ^{∞} is 3.5% for all solutes. [b] Due to the large retention times of the xylenes at 293.44 K, the activity coefficients at infinite dilution could not be measured.

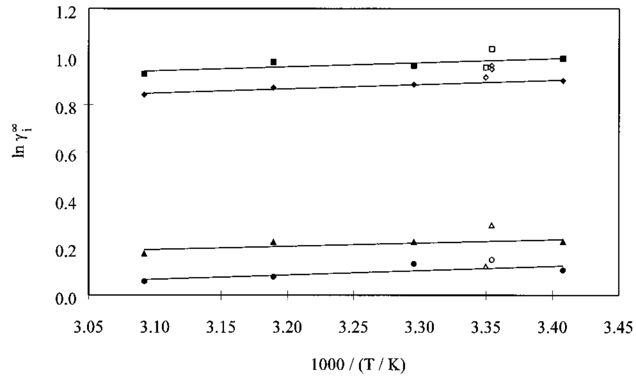

Figure 2. Activity coefficients at infinite dilution, γ_i^{∞}, for four solutes in the solvent 1-octanol as a function of temperature. This work: (◆) pentane; (■) hexane; (●) 1-propanol; (▲) methanol; (—) linear regression. Published values: (◇) pentane, Kohn (1988), Tewari et al. (1982), Tse and Sandler (1994); (□) hexane, Kohn (1988), Tewari et al. (1982); (○) 1-propanol, Dallas static method (1995); (△) methanol, Dallas static method (1995), Kohn (1988).

Taking into account that the Antoine constants taken from the DDB to calculate the saturation vapor pressure and the determination of K_L in the presence of adsorption effects are also subject to an error, the resulting error in the γ^{∞} is

$$S_{\gamma^{\infty}} = 3.5\% \qquad (7)$$

Figures 2 and 3 show examples of the linear relationship between the natural logarithm of the activity coefficient and the inverse absolute temperature for selected solutes in 1-octanol. The graphs additionally contain γ^{∞} data taken from the literature which were obtained by either GLC or static techniques. The results presented here show better agreement to the data obtained by a static method than to measurements using the GLC technique. One reason for this could be due to the correction made in this work for the contribution of adsorption at the gas–liquid interface to the γ^{∞}. A consideration of adsorption effects was not mentioned by the other authors. For this reason the γ^{∞} values determined in this work were lower than those

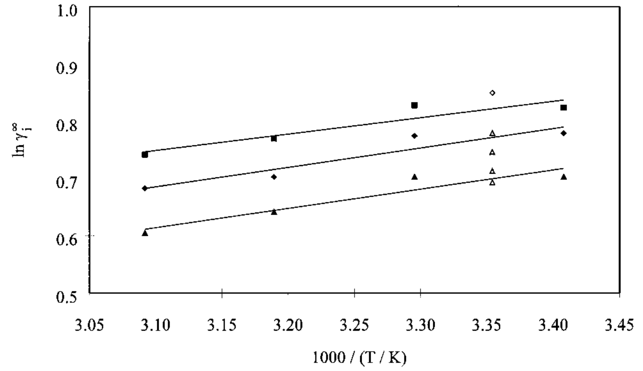

Figure 3. Activity coefficients at infinite dilution, γ_i^∞, for four solutes in the solvent 1-octanol as a function of temperature. This work: (◆) cyclohexane; (■) methylcyclohexane; (▲) toluene; (—) linear regression. Published values: (◇) cyclohexane, Tse and Sandler (1994); (△) toluene, Hussam et al. static method (1985), Park et al. static method (1987), Tewari et al. (1982), Dallas static method (1995).

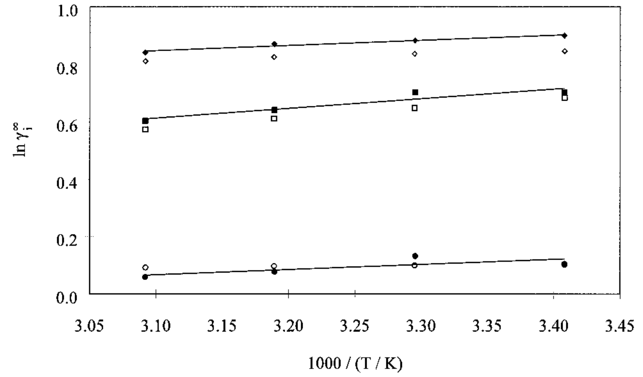

Figure 4. Activity coefficients at infinite dilution, γ_i^∞, for three solutes in the solvent 1-octanol as a function of temperature. This work: (◆) 1-propanol; (■) toluene; (●) pentane; (—) linear regression. Predicted values using modified UNIFAC (Do) (Gmehling et al., 1993): (◇) 1-propanol; (□) toluene; (○) pentane.

found by GLC in the literature. In the case of the alcohols studied in this work, the activity coefficients tend to decrease with increasing molecular weight. The opposite effect is observed for the hydrocarbon and cyclic hydrocarbon series. The graph often shows a straight line in a limited temperature interval. Figure 4 compares activity coefficients at infinite dilution obtained in this work with predicted values calculated by the modified UNIFAC (Do) equation (Gmehling et al., 1993). The graph shows that the predicted values are in accordance with the experimental data.

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 line

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial \frac{1}{T}}\right)_{P,x} = \frac{H_i^{E,\infty}}{R} \tag{8}$$

For most of the solutes measured in this work, it is clear that the limiting activity coefficients tend toward ideal behavior ($\gamma^\infty = 1$) as the temperature increases. The temperature dependence found by the gas chromatographic method is confirmed by data given in the DECHEMA Chemistry Data Series (Christensen et al., 1991). The absolute degree of exactness of the partial molar excess enthalpy at infinite dilution depends to a great extent on the quality of the measured experimental γ^∞ and on the temperature range of the measurements. It is evident that, in particular for systems where the slope of the straight line is satisfactory large, a satisfactory to good reproduction of the partial molar excess enthalpy at infinite dilution is possible despite the errors associated with GLC measurements. The estimated error in $H_i^{E,\infty}$ is about 35% (Schiller, 1993). However a criterion for the reliability of the data determined here can be seen in the reproduction of the direction of the temperature dependence of the limiting activity coefficient which can be recognized from the sign of the partial molar excess enthalpy H_i^E.

Conclusion

Activity coefficients of various solutes in 1-octanol at infinite dilution have been measured at four different temperatures by GLC. GLC is a fast and reliable technique. Adsorption effects at the gas−liquid interface have been taken into account using the method proposed by Conder et al. to obtain γ^∞ without adsorption. By applying thermodynamic principles (i.e. the Gibbs−Helmholtz equation), the reliability of the data measured was checked using partial molar excess enthalpy data.

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