

Infinite Dilution Activity Coefficients of Organic Solutes in *N,N*-Diethyldodecanamide

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Infinite dilution activity coefficients of pentane, hexane, heptane, cyclohexane, benzene, tetrachloromethane, dichloromethane, diethyl ether, tetrahydrofuran, acetone, ethyl acetate and methanol in *N,N*-diethyldodecanamide have been measured using gas-liquid chromatography. The measurements have been performed at 25, 35, 45 and 55 °C. The solute partial molar excess enthalpies and entropies at infinite dilution have been calculated from the temperature dependence of the activity coefficients. Experimental values of activity coefficients at infinite dilution were compared with predictions based on the UNIFAC model.

Introduction

The activity coefficient is a fundamental thermodynamic property of solution as it gives a measure of the deviation from Raoult's law for a particular liquid mixture. A knowledge of the activity coefficient at infinite dilution (γ^∞) is important since solution behavior is clearly expressed at infinite dilution. These boundary values of activity coefficients are of great importance for development of solution theories and improvements in the simulation of separation processes, especially in the production of very pure substances. Vapor-liquid equilibria can be predicted if γ^∞ values for both components of a binary solution are known. Also, experimental values of γ^∞ enable extension of the present databases for the further development of group contribution methods (1, 2).

N-substituted amides have been attracting considerable attention, mainly due to their importance in biochemistry (3-5). However, there has been less work on the thermodynamics of binary liquid mixtures of this class of compounds (6-8).

Gas-liquid chromatography is an effective and advantageous technique for studying the equilibrium properties of nonelectrolytic solutions in which one component is at infinite dilution (9, 10).

Theoretical Background

The specific retention volume V_g^0 corrected to 0 °C is related to the experimental variables (9, 11)

$$V_g^0 = t_R' \bar{F}_c^0 / m_1 \quad (1)$$

where t_R' is the solute retention time corrected for dead space and m_1 is the mass of the solvent in the column. The volume flow rate of the carrier gas adjusted to the mean column pressure and 0 °C is given as

$$\bar{F}_c^0 = FJ \left(\frac{p_{fm} - p_w^0}{p_0} \right) \left(\frac{273.15}{T_{fm}} \right) \quad (2)$$

with the James-Martin (12) factor J ,

Table 1. Specific Retention Volumes of Solutes in *N,N*-Diethyldodecanamide

solute	$V_g^0 / (\text{cm}^3 \cdot \text{g}^{-1})$			
	$t = 25 \text{ }^\circ\text{C}$	$t = 35 \text{ }^\circ\text{C}$	$t = 45 \text{ }^\circ\text{C}$	$t = 55 \text{ }^\circ\text{C}$
pentane	109.3	78.09	57.27	42.94
hexane	341.2	231.0	161.5	115.6
heptane	1075	678.9	445.0	301.0
cyclohexane	673.4	448.7	309.6	218.5
benzene	1190	768.1	513.7	354.2
tetrachloromethane	1060	682.1	453.5	310.4
dichloromethane	656.0	425.5	285.5	197.4
diethyl ether	135.1	95.62	69.64	51.86
tetrahydrofuran	635.2	422.2	289.7	204.2
acetone	258.7	176.0	123.6	89.11
ethyl acetate	612.8	400.1	270.3	189.3
methanol	778.9	468.1	290.5	186.4

$$J = \frac{3}{2} \left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right] \quad (3)$$

and where F is the volume flow rate of the carrier gas in the soap-bubble flowmeter at temperature T_{fm} and pressure p_{fm} , p_w^0 is the saturation vapor pressure of water at T_{fm} , and p_i and p_0 are, respectively, the column inlet and outlet pressures.

The solute activity coefficient at infinite dilution γ_2^∞ can be obtained from the specific retention volume (11, 13),

$$\ln \gamma_2^\infty = \ln(273.15R/M_1 f_2^0 V_g^0) \quad (4)$$

where M_1 is the molar mass of the solvent. The saturation fugacity of the solute at temperature T , f_2^0 , is defined as

$$\ln f_2^0 = \ln p_2^0 + (B_{22} p_2^0 / RT) \quad (5)$$

where p_2^0 and B_{22} are the saturated vapor pressure and second virial coefficient of the pure solute at the column temperature T , respectively.

The temperature dependence of γ_2^∞ is given as

$$\ln \gamma_2^\infty = \frac{H_2^{E^\infty}}{RT} - \frac{S_2^{E^\infty}}{R} \quad (6)$$

where $H_2^{E^\infty}$ and $S_2^{E^\infty}$ are the solute partial molar excess enthalpy and entropy at infinite dilution, respectively.

Experimental Section

The solvent (stationary phase) *N,N*-diethyldodecanamide (DEDA) was supported on Chromosorb G (acid washed and

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Table 2. Solute Activity Coefficients and Partial Molar Excess Enthalpies and Entropies at Infinite Dilution in *N,N*-Diethyldodecanamide

solute	γ_2^∞				$H_2^{E\infty}/(\text{kJ}\cdot\text{mol}^{-1})$	$S_2^{E\infty}/(\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$
	$t = 25^\circ\text{C}$	$t = 35^\circ\text{C}$	$t = 45^\circ\text{C}$	$t = 55^\circ\text{C}$		
pentane	1.230	1.216	1.203	1.192	0.85	1.1
hexane	1.313	1.285	1.256	1.234	1.70	3.4
heptane	1.367	1.344	1.322	1.303	1.30	1.8
cyclohexane	1.014	0.990	0.965	0.947	1.88	6.2
benzene	0.600	0.597	0.594	0.591	0.41	5.6
tetrachloromethane	0.556	0.567	0.578	0.589	-1.56	-0.4
dichloromethane	0.241	0.255	0.268	0.280	-4.07	-1.8
diethyl ether	0.956	0.946	0.935	0.926	0.87	3.3
tetrahydrofuran	0.655	0.649	0.643	0.638	0.72	5.9
acetone	1.143	1.119	1.095	1.073	1.72	4.6
ethyl acetate	1.163	1.122	1.085	1.045	2.88	8.4
methanol	0.678	0.686	0.695	0.702	-0.95	<0.1

DMCS treated, 60–80 mesh) and packed in stainless steel tubings (75 cm \times 6.1 mm i.d.). DEDA was a commercial product (Aldrich) and was purified by distillation under reduced pressure (166 $^\circ\text{C}$, 266.644 Pa). The purity of the solvent was determined by GLC-MS and was better than 99 mol %.

The solutes (reagent grade, Fluka) were used without further purification, since solute purity is not important in these measurements.

A Varian gas chromatograph, model 1860, modified for precise thermodynamic measurements, and a thermal-conductivity detector were employed. The columns were placed in a thermostated water bath where the temperature could be maintained to $\pm 0.05^\circ\text{C}$. The inlet pressure of the carrier gas (hydrogen) was measured with a precision mercury manometer. The outlet pressure was taken as the atmospheric. The volume flow rate of the carrier gas was measured with a thermostated soap-bubble flowmeter, at the detector outlet.

For all solutes, the chromatographic peaks were symmetrical, indicating that the solutions obeyed Henry's law. Solutes were injected as a mixture of air and solute-saturated vapor in a volume of 5 μL .

The ashing method was utilized to determine the exact solvent percentage in the column packing, taking into account the bare-support mass loss due to decomposition of the silanized surface (14, 15). Since the ashing of the column packing was performed twice, before and after the experiments, it was possible to establish the absence of any significant column bleeding at the experimental temperatures.

To examine possible effects of interfacial adsorption (16, 17), four different stationary-phase loadings (in the range 3–12 mass %) were prepared. The experiments made on these columns showed that specific retention volumes of all solutes were independent of liquid-phase loading.

Results and Discussion

The specific retention volumes are listed in Table 1. It was shown that the relative random error in V_g^0 may be estimated from those in the experimental variables through propagation-of-error analysis (8, 13, 15),

$$\left[\frac{\sigma(V_g^0)}{V_g^0} \right] = \left\{ \left[\frac{\sigma(t_R')}{t_R'} \right]^2 + \left[\frac{\sigma(\bar{F}_c^0)}{\bar{F}_c^0} \right]^2 + \left[\frac{\sigma(m_1)}{m_1} \right]^2 \right\}^{1/2} \quad (7)$$

As the total mass of column packing is known to high precision, the error in m_1 is actually governed by the error associated with determination (by ashing) of the mass per cent of stationary phase present in the packing. Taking into account the percent standard deviations estimated in multiple measurements of t_R' (0.30%), \bar{F}_c^0 (0.19%), and m_1 (0.65%), the relative standard deviation of the specific retention volume

Table 3. Comparison between Experimental and Predicted Values of Activity Coefficients at Infinite Dilution in *N,N*-Diethyldodecanamide Using the UNIFAC Model at 25 $^\circ\text{C}$

solute	$\gamma_2^{\infty\text{exp}}$	$\gamma_2^{\infty\text{calc}}$	rel dev/%
pentane	1.230	0.787	35.8
hexane	1.313	0.897	31.0
heptane	1.367	1.001	26.2
cyclohexane	1.014	0.801	20.0
benzene	0.600	0.463	22.6
tetrachloromethane	0.556	0.495	11.9
dichloromethane	0.241	0.398	59.8
diethyl ether	0.956	0.636	33.2
tetrahydrofuran	0.655	0.669	2.6
acetone	1.143	1.073	5.3
ethyl acetate	1.163	0.941	17.7
methanol	0.678	0.917	34.4

is calculated to be 0.74%. As was also noticed in previous studies (8, 13, 15), the dominant error is the uncertainty in m_1 .

The solute activity coefficients at infinite dilution for four experimental temperatures are listed in Table 2. The saturation vapor pressures of solutes were calculated from the Antoine equation using constants from Boublik's compilation (18). The second virial coefficients were obtained on the basis of the experimental B_{22} values collected by Dymond and Smith (19).

The relative standard deviation of γ_2^∞ was estimated from those of V_g^0 and f_2° (8, 13),

$$\left[\frac{\sigma(\gamma_2^\infty)}{\gamma_2^\infty} \right] = \left\{ \left[\frac{\sigma(V_g^0)}{V_g^0} \right]^2 + \left[\frac{\sigma(f_2^\circ)}{f_2^\circ} \right]^2 \right\}^{1/2} \quad (8)$$

Since the relative standard deviation of fugacity, obtained from the reported uncertainties in p_2° and B_{22} , did not exceed 0.2%, the resulting $\sigma(\gamma_2^\infty)/\gamma_2^\infty$ was about 0.008.

Linear regression analysis of $\ln \gamma_2^\infty$ as a function of $1/T$ yielded the $H_2^{E\infty}$ and $S_2^{E\infty}$ values listed in Table 2. The correlation coefficients of the linear regression were all better than 0.999, and the average uncertainties in $H_2^{E\infty}$ and $S_2^{E\infty}$ were 0.04 $\text{kJ}\cdot\text{mol}^{-1}$ and 0.1 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively. Both uncertainties are based on the standard deviations of the slope and ordinate intercept in eq 6.

The infinite dilution activity coefficient γ_2^∞ calculated from the UNIFAC group contribution model (1, 20) was compared with the experimental γ_2^∞ in Table 3. A mean deviation of 25% was obtained for all solutes, and it is of the same order of magnitude (or even less) than the reported deviations for many other solutions (21, 22).

Glossary

B_{22} second virial coefficient of the solute, $\text{cm}^3\cdot\text{mol}^{-1}$

f_2°	saturation fugacity of the solute
F	volume flow rate of the carrier gas, cm^3s^{-1}
\bar{F}_c^0	volume flow rate of the carrier gas adjusted to mean column pressure and 0°C
$H_2^{E\infty}$	solute partial molar excess enthalpy at infinite dilution, $\text{kJ}\cdot\text{mol}^{-1}$
J	James-Martin factor
m_1	mass of the solvent in the column, g
M_1	molar mass of the solvent, $\text{g}\cdot\text{mol}^{-1}$
p_{fm}	pressure at the flowmeter, mmHg
p_o	column outlet pressure
p_i	column inlet pressure
p_w°	saturation vapor pressure of water
p_2°	saturation vapor pressure of solute
$S_2^{E\infty}$	solute partial molar excess entropy at infinite dilution, $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
t_R'	retention time corrected for dead space, s
T	column temperature, K
T_{fm}	temperature of the flowmeter
V_g^0	specific retention volume corrected to 0°C , $\text{cm}^3\cdot\text{g}^{-1}$

Greek Letters

γ_2°	solute activity coefficient at infinite dilution
$\sigma(i)$	standard deviation of the i variable

Registry Numbers Supplied by Authors. DEDA, 3352-87-2; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; cyclohexane, 110-827; benzene, 71-43-2; tetrachloromethane, 56-23-5; dichloromethane, 75-09-2; diethyl ether, 60-29-7; tetrahydrofuran, 109-99-9; acetone, 67-64-1; ethyl acetate, 141-78-6; methanol, 67-56-1.

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