Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in Glycerol Using Gas−Liquid Chromatography

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The activity coefficients at infinite dilution, γ_i^∞, for 16 organic solutes, alkanes, alkenes, and alkyl benzenes in glycerol, have been measured by the gas−liquid chromatographic method at five temperatures from (303.15 to 343.15) K. The overall uncertainty was estimated to be about 5 %. The partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, of the solutes in glycerol were also derived from the temperature dependence of the γ_i^∞ values.

Introduction

Glycerol (1,2,3-propanetriol, also glycerin or glycerine) is a potentially important biorefinery feedstock.[1] Crude glycerol is a major byproduct for the biodiesel industry by transesterification of vegetable oils or animal fats.[1−3] Widespread application of the glycerol mixtures has been found in the manufacturing of solvents because it is nontoxic and possesses good solvent properties for many compounds. Activity coefficients at infinite dilution, γ_i^∞, of organic solutes (*i*) are a good source of data to quantify the selectivity and solvent power of solvents and to gain information on the molecular interactions between solvents and organic solutes.[4,5] Experimental γ_i^∞ data provide valuable information for testing predictive models.[6] A number of experimental techniques are available for direct measurement of γ_i^∞, including steady-state gas−liquid chromatography (GLC),[7] the dilutor technique (DT method) or inert gas stripping,[8] differential ebulliometry,[9] headspace,[10] and dew point techniques.[11] Each of these techniques has some limitations.[12] The GLC method is fast and accurate and requires only a small amount of the required agent. The use of a GLC technique for the determination of γ_i^∞ has been employed by many researchers and has proved quite reliable.[13]

In this paper, γ_i^∞ have been measured for 16 organic solutes: alkanes (hexane, heptane, octane, nonane, decane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane), alkenes (cyclohexene and styrene), and alkyl benzenes (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene) in glycerol by the GLC method. The measurements were carried out in the temperature range of (303.15 to 343.15) K. The partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, of the solutes in glycerol at 298.15 K were also derived from the temperature dependence of the γ_i^∞ values.

Experimental Section

Materials. The glycerol and the 16 organic solutes including alkanes, alkenes, and alkyl benzenes were purchased from different suppliers. Their mass fraction purities were greater than 0.99. The glycerol was distilled before use, and water mass fractions analyzed by Karl Fischer analysis were less than 10^{-3}. All precautions were taken to minimize its exposure to air as it is extremely hygroscopic. The organic solutes were used without further purification.

Apparatus and Procedure. The experiments were performed on a Varian Chrompack CP-3800 GC equipped with a thermal conductivity detector. The column preparation and the packing method used in this work have been described previously.[14] The GC columns used were 100 cm in length and 0.40 cm in inner diameter. The solid support is an 80-100 mesh Chromosorb W, acid-washed and silanized. Coating the solid support with pure glycerol was performed by dispersing a known mass amount of the Chromosorb in a solution of glycerol in ethanol followed by evaporation of the solvent in a rotating evaporator. The Chromosorb was weighed on an electronic balance of precision of ± 0.0001 g before and after the coating process. Two columns were used at 323.15 K to check for the reliability of the results. The mass fraction of glycerol was about 30 % of the support material. The column was filled uniformly with the help of an ultrasound vibrator and finally heated under nitrogen for 6 h at the column temperature of 60 °C. To avoid the loss of the stationary phase in the column, a saturation vessel that contains the same liquid as the stationary phase was placed in front of the column.

Dry nitrogen was used as the carrier gas. The flow rate of carrier gas was determined using a calibrated soap bubble flowmeter which was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least 15 min before any γ_i^∞ determinations were made. The volume of the samples injected into the GC probes was about (0.02 to 0.5) μL, and the peaks were found to be symmetrical, independent of the carrier gas flow rate. The retention time of each injected component was collected using Workstation software. The experiments were carried out over a temperature range from (303.15 to 343.15) K. The temperature of the GC column was maintained constant within ± 0.05 K. At a given temperature, each operation was repeated at least three times to check the reproducibility. The deviation of the retention time of the three measurements was within (0.01 to 0.03) min. The value of the dead time was determined with methane as the nonretainable pure component under the assumption that the effect of the solubility of methane in glycerol

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was negligible. This assumption has been justified by confirmation of our experimental procedure with the reliable γ_i^{∞} values of hexane in hexadecane at 313.15 K, and the results compared very favorably with the literature values.[15] The measured dead time in the temperature range has a deviation of ± 0.01 min.

The outlet pressure p_0 was kept equal to the atmospheric pressure. The pressure drop was recorded by GC and automatically measured using a membrane manometer with an uncertainty of ± 0.2 kPa. To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the carrier gas stream, the measurements of retention time were repeated systematically every (6 to 8) h for hexane and benzene. No change of the retention time was observed during 80 h of continuous operation.

Theoretical Basis. Cruickshank et al.[16] and Everett[17] developed the following equation for obtaining the activity coefficients at infinite dilution for a volatile solute (i) in an involatile solvent (3):

$$\ln \gamma_{i,3}^{\infty} = \ln\left(\frac{n_3RT}{V_{\mathrm{N}}p_i^0}\right) - \frac{B_{11} - V_i^0}{RT}p_i^0 + \frac{2B_{12} - V_i^{\infty}}{RT}Jp_0 \tag{1}$$

In eq 1, $\gamma_{i,3}^{\infty}$ is the activity coefficient of solute i at infinite dilution in the stationary phase (3), p_i^0 is the vapor pressure of the pure liquid solute i, n_3 is the number of moles of the stationary phase component on the column, and V_{N} is the standardized retention volume obtained by eq 2.

$$V_{\mathrm{N}} = JU_0(t_{\mathrm{r}} - t_{\mathrm{G}})\frac{T_{\mathrm{col}}}{T_{\mathrm{f}}}\left[1 - \frac{p_{\mathrm{w}}^0}{p_0}\right] \tag{2}$$

where t_{r} denotes the retention time, t_{G} the dead time, U_0 the flow rate of the carrier gas, T_{col} the column temperature, T_{f} the flow-meter temperature, p_{w}^0 the saturation vapor pressure of water at T_{f}, and p_0 the pressure at the column outlet.

The second and third terms in eq 1 are correction terms arising from the nonideality of the mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{12} the cross second virial coefficient of the solute (1) with the carrier gas (2), V_i^0 the liquid molar volume of pure solute, and V_i^{∞} the partial molar volume of the solute in the stationary phase (3) at infinite dilution.

The data for calculating the correction terms have been obtained in the following way. For all solutes, values of p_i^0 were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.[18] Molar volumes of solutes V_i^0 were estimated using their experimental densities;[19] partial molar volumes of solute at infinite dilution V_i^{∞} have been assumed to be equal to V_i^0. B_{11} and B_{12} have been estimated according to the equations suitable for nonpolar liquids by Tsonopolous's method.[20] Critical parameters needed for the calculations were available from the literature.[20] The cross critical properties P_{cij}, T_{cij}, V_{cij}, Z_{cij}, and acentric factor ω_{ij} were calculated by using equations given in the literature.[20,21]

The pressure correction term J is given by[22]

$$J = \frac{3}{2}\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \tag{3}$$

where p_i and p_0 are the inlet and outlet pressures of the GC column, respectively.

Retention time, dead time, column temperature, flow rate, input and output pressure, and the mass of stationary phase all have experimental errors. The uncertainties in the measured and derived quantities are listed in Table 1. From a propagation of error analysis, and taking into account that thermodynamic parameters are also subject to an error, the γ_i^{∞} values in this work are estimated to have an uncertainty within ± 5 %.

Table 1. Relative Uncertainties in the Measured and Derived Quantities

parameters	relative uncertainty
$(t_{\mathrm{r}} - t_{\mathrm{G}})$/min	± 2.7 %
U_0/mL·min^{-1}	± 0.5 %
p_i/kPa	± 0.6 %
p_0/kPa	± 0.02 %
J	± 1 %
p_i^0/kPa	± 0.01 % to ± 0.25 %
n_3/mol	± 0.5 %
γ_i^{∞}	± 5 %

Table 2. Experimental Activity Coefficients at Infinite Dilution, γ_i^{∞}, for Various Solutes in Glycerol at Temperatures of (303.15 to 343.15) K

	γ_i^{∞}				
solutes (i)	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15
Alkanes					
hexane	414	383	340	316	268
heptane	580	527	450	386	304
octane	677	601	511	445	379
nonane	846	752	691	640	559
decane	1046	881	798	701	612
cyclohexane	232	204	181	166	145
methylcyclohexane	281	264	239	203	183
2,2,4-trimethylpentane	636	585	497	406	329
Alkenes					
cyclohexene	183	156	126	110	88.4
styrene	125	103	81.7	61.5	44.5
Alkyl Benzenes					
benzene	60.1	55.9	51.1	45.1	37.9
toluene	128	111	91.1	76.1	60.0
ethylbenzene	162	141	120	102	89.7
o-xylene	139	121	98.8	83.7	68.5
m-xylene	147	127	106	93.2	76.1
p-xylene	155	131	115	100	85.0

Results and Discussion

Experimental results of γ_i^{∞} for 16 solutes in glycerol at different temperatures are presented in Table 2. The exceptionally high values for the alkanes are most likely due to the large disparity in the chemical nature of the solvent and solute. The γ_i^{∞} values for the linear *n*-alkanes increase with increasing chain length. The branching of the alkane skeleton (e.g., cyclohexane, methylcyclohexane, or 2,2,4-trimethylpentane) reduces the values of γ_i^{∞} in comparison with the corresponding linear alkanes: hexane, heptane, and octane. Introduction of the double bond in the six-membered ring (cyclohexene) causes a reduction of γ_i^{∞}.

For the aromatic compounds, the values of γ_i^{∞} are distinctly lower in comparison with those of the alkanes, and the values of γ_i^{∞} increase with the increasing size of the alkyl group. The smallest values indicate stronger interactions between solvent and solute. It means that the hydroxyl groups of glycerol can form stronger interactions with the aromatic solutes. Experimental results of γ_i^{∞} at different temperatures were correlated with temperature by the following equation:

$$\ln \gamma_i^{\infty} = a + \frac{b}{(T/\mathrm{K})} \tag{4}$$

The coefficients a and b, the standard deviation σ of the fitted equations, and the values of γ_i^{∞} at 298.15 K are listed in Table

Table 3. Coefficients *a* and *b* of Equation 4, γ_i^∞ at 298.15 K Calculated Using Equation 4, Values of $H_i^{E,\infty}$ Derived from Equation 5, and Standard Deviation *σ*

solute (*i*)	*a*	$\frac{b}{K}$	$\gamma_i^\infty{}_{298.15K}$	$\frac{H_i^{E,\infty}}{kJ\cdot mol^{-1}}$	*σ*
Alkanes					
hexane	2.4353	1094.80	449	9.10	0.031
heptane	0.9444	1657.32	667	13.8	0.055
octane	1.5396	1515.45	752	12.6	0.021
nonane	3.3593	1025.15	896	8.52	0.020
decane	2.4809	1353.38	1119	11.3	0.017
cyclohexane	1.5268	1188.28	248	9.88	0.012
methylcyclohexane	1.8351	611.90	48.8	5.09	0.036
2,2,4-trimethylpentane	0.7730	1739.79	741	14.5	0.058
Alkenes					
cyclohexene	−0.9562	1874.68	207	15.6	0.028
styrene	−3.9046	2663.81	153	22.2	0.066
Alkyl Benzenes					
benzene	0.2560	1175.04	66.5	9.77	0.045
toluene	−1.5928	1965.12	148	16.3	0.039
ethyl benzene	−0.0521	1561.72	179	13.0	0.014
o-xylene	−1.1613	1856.98	159	15.4	0.028
m-xylene	−0.5523	1685.23	164	14.0	0.026
p-xylene	−0.0054	1531.85	169	12.7	0.015

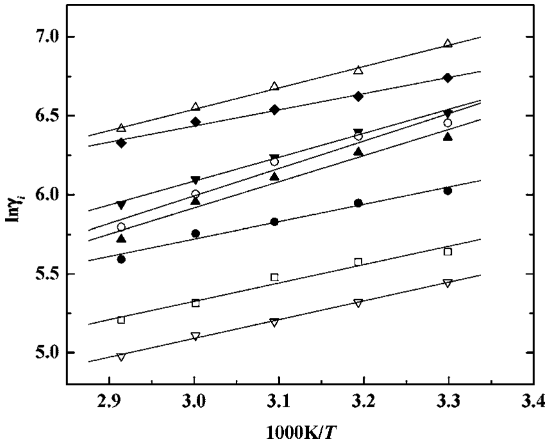

Figure 1. Plot of ln γ_i^∞ vs 1/*T* for the solutes together with a linear correlation of the data: ●, hexane; ▲, heptane; ▼, octane; ◆, nonane; △, decane; ▽, cyclohexane; □, methylcyclohexane; ○, 2,2,4-trimethylpentane; —, linear correlation.

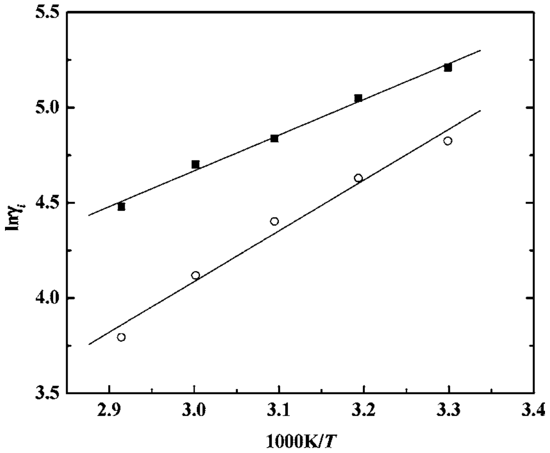

Figure 2. Plot of ln γ_i^∞ vs 1/*T* for the solutes together with a linear correlation of the data: ■, cyclohexene; ○, styrene; —, linear correlation.

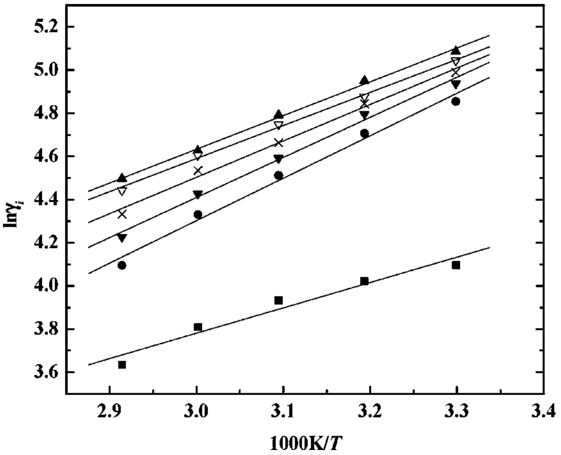

Figure 3. Plot of ln γ_i^∞ vs 1/*T* for the solutes together with a linear correlation of the data: ■, benzene; ●, toluene; ▼, *o*-xylene; ×, *m*-xylene; ▽, *p*-xylene; ▲, ethyl benzene; —, linear correlation.

Table 4. Selectivity Values, S_{ij}^∞, of Various Solvents for the Separation of Hexane (*i*)/Benzene (*j*) Mixture at 303.15 K

solvent	S_{ij}^∞
glycerol	6.89
N-methylformamide	8.25[24]
N-methyl-2-pyrrolidone	12.6[25]
dimethyl sulfoxide	20.4[26]
sulfolane	19.8[27]

3. The plots of measured ln γ_i^∞ versus 1/*T* values and the linear fit of their data are given in Figures 1 to 3, which show a fairly good fitting quality of eq 4. According to the Gibbs−Helmholtz equation, the partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, can be directly obtained from the slope of a straight line derived from eq 5:

$$\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)} = \frac{H_i^{E,\infty}}{R} \tag{5}$$

where *R* is the gas constant. The values of $H_i^{E,\infty}$ for the solutes studied are also listed in Table 3. For the linear alkanes, cyclohexene, and alkyl benzenes $H_i^{E,\infty}$ all have positive values. The relative uncertainties of $H_i^{E,\infty}$ are about ± 10 %.

The selectivity S_{ij}^∞ is defined as $S_{ij}^\infty = \gamma_{i3}^\infty/\gamma_{j3}^\infty$.[23] It indicates the suitability of a solvent for separating mixtures of components *i* and *j* by extraction. The values of selectivity S_{ij}^∞ for the separation of a hexane (*i*)/benzene (*j*) mixture are listed in Table 4 together with the literature values[24−27] of conventional solvents. The results indicated that glycerol would not serve as an ideal extraction solvent for the separation of aliphatic and aromatic mixtures. The values of S_{ij}^∞ for three isomeric xylenes at 298.15 K were 1.03 (*m*-xylene/*o*-xylene), 1.03 (*p*-xylene/*m*-xylene), and 1.07 (*p*-xylene/*o*-xylene), respectively. The results indicated that glycerol was not an ideal extraction solvent for the separation of xylenes.

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