Infinite Dilution Activity Coefficients in Tributyl Phosphate and Triacetin

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Experimental data on infinite dilution activity coefficients of hydrocarbons, chlorinated hydrocarbons, alcohols, ethers, and ketones in triacetin and tributyl phosphate are presented. The measurements were made by inverse gas chromatography. A temperature range between 323 K and 353 K was covered. The solubility parameters of tributyl phosphate and triacetin were determined from the experimental data.

Introduction

Tributyl phosphate and triacetin are extensively used as solvents in the extractive industry. Due to its physicochemical properties, tributyl phosphate is also used as hydraulic fluid in modern aircraft. Because of its toxicity, its presence has to be monitored and its concentration kept as low as possible. There is little information in the literature about the solvent properties of esters, such as tributyl phosphate and triacetin.

The measurement of infinite dilution activity coefficients (γ^∞) by gas−liquid chromatography is an adequate technique to study the solvent properties of low vapor pressure compounds. The technique consists of measuring the retention volume of a given solute in a stationary phase prepared by coating an inert solid support with the high-boiling solvent. By careful preparation of the chromatographic column, reproducible data can be obtained in a short period of time, using extremely small amounts of solutes. Experiments should be done under isothermal conditions, since activity coefficients are temperature dependent. Elution times, eluent flow rate, and stationary phase mass must also be carefully measured.

Infinite dilution data measure the maximum deviation of a solute from the Lewis−Randall ideal solution limit and give a good insight into solute−solvent molecular interactions. The data can be used to explore the application of group contribution predictive methods such as UNIFAC and ASOG and to estimate solvent properties for extraction processes.

Experimental Section

The infinite dilution activity coefficients were measured by inverse gas−liquid chromatography.[1] Details of the experimental technique and calculations are given in previous publications.[2,3]

The calculation of γ^∞ requires the measurement of the following variables: (a) net retention time ($t_i - t_0$) of the solute, that is, the difference between the retention times of solute (i) and inert gas (0); (b) column temperature T; (c) column inlet pressure P_I and outlet pressure P_0; (d) carrier gas flow rate F measured at temperature T_f and pressure P_f; (e) mass w_s of solvent contained within the column.

From these experimental data, the retention volume V_g° and infinite dilution activity coefficient γ_i^∞ were calculated by means of a computer program (GLC, University of Trieste). The James−Martin correction factor J_3^2 for the pressure gradient and gas compressibility inside the column was applied in the calculation of V_g°;[4] gas-phase nonidealities were taken into account by means of the virial equation of state.

$$V_g^\circ = F(273.15/T_f)(t_i - t_0)((P_f - P_w^s)/P_0)J_3^2/w_s \qquad (1)$$

$$\ln \gamma_i^\infty = \ln(273.15R/(M_s P_i^s V_g^\circ)) - (B_{ii} - v_i)P_i^s/(RT) \qquad (2)$$

In these equations P_w^s and P_i^s are, respectively, the vapor pressure of water at temperature T_f and that of organic solute i at column temperature T; B_{ii} and v_i are the second virial coefficient and the liquid molar volume of solute i at temperature T; M_s is the molecular weight of the solvent; and R is the universal gas constant.

A Varian 3400 Cx gas chromatograph with an FID detector and a Hewlett-Packard 3392 integrator was used in the measurements. The carrier gas was hydrogen flowing at about 30 cm^3/min. The flow rates were measured with a soap-film meter, and temperatures, with a platinum resistance thermometer (Systemteknik AB S1220). The column outlet pressure was determined with a quartz transducer (Paroscientific), and the pressure drop inside the column (450−500 mbar) was read with a cathetometer from a U tube mercury manometer.

The stationary phase for each column was prepared by mixing with chloroform known masses of solvent (triacetin or tributyl phosphate) and inert support (Chromosorb W60/80 mesh, Johns Manville). A ratio of three parts of chromosorb to one part of solvent was used. Chloroform was then slowly evaporated from the mixture, in a rotary evaporator at low temperature (30 °C) and under a dry nitrogen atmosphere. Stainless steel tubing, $^1/_8$ in. external diameter by 1 m or 2 m long, was filled with the stationary phase. The amount of stationary phase inside the column was determined gravimetrically.

The uncertanties in the measured variables were estimated to be ±1 cm^3/min for the carrier gas flow; ±0.1 K for the temperatures; ±3 mbar for the inlet pressure; ±0.1 mbar for the outlet pressure; and ±0.1 mg for the mass of solvent in the column.

All chemicals were used as provided by vendors, without further purification. Triacetin was gold label, 99% purity, from Aldrich Chemical Co., and tributyl phosphate was

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Table 1. Infinite Dilution Activity Coefficients (γ^∞) in Tributyl Phosphate

	γ^∞			
solute	$T = 298.15$ K from literature[6]	$T = 324.9$ K column 2 m long	$T = 324$ K column 1 m long	$T = 343.7$ K
pentane		1.60		1.59
hexane	1.70	1.75	1.73	1.72
heptane	1.96	1.94	1.91	1.88
2,2,4-trimethylpentane		2.02	2.01	1.97
cyclohexane	1.45	1.34	1.33	1.33
1-hexene		1.31	1.28	1.33
benzene	0.60	0.61	0.61	0.64
toluene			0.71	0.75
ethylbenzene			2.37	
ethanol		0.50	0.49	0.51
2-propanol			0.48	
acetone		0.86	0.84	
methyl ethyl ketone			0.77	0.88
ethyl acetate		0.91	0.90	0.93
chloroform	0.12	0.12	0.12	0.16
trichloroethylene		0.40	0.40	0.47
1,2-dichloroethane		0.36	0.36	0.42
carbon tetrachloride	0.63	0.64	0.65	0.69

Table 2. Infinite Dilution Activity Coefficients in Triacetin

	γ^∞		
solute	$T = 323$ K	$T = 343$ K	$T = 353$ K
heptane	11.84	9.40	8.90
hexane	9.28	8.15	7.04
cyclohexane	5.79	5.10	4.81
1-hexene	5.21	4.79	4.60
benzene	1.21	1.26	1.21
toluene	1.63	1.66	1.59
methanol		1.58	
ethanol	2.05	1.80	1.59
1-propanol	2.21	1.91	1.70
2-propanol	2.17	1.88	1.69
1-butanol		2.22	2.06
2-butanol	2.17		1.78
chloroform	0.54	0.62	0.62
1,2-dichloroethane	0.72	0.75	0.75
trichloroethylene	1.32	1.34	1.30
chlorobenzene		1.13	1.35
ethyl ether	2.05	1.93	1.96
methyl *tert*-butyl ether	3.01	2.74	2.70
isopropyl ether	3.24	3.47	3.40
butyl ether		5.54	5.66
ethyl acetate	1.05	1.04	1.10
methyl ethyl ketone	0.90	1.06	1.10
anisol			3.43
acetone	0.94	0.99	0.98

analytical grade, 99% purity, from Anedra. The solutes were chromatographic or reagent grade compounds. Since GLC is itself a separation technique, the experimental results are not influenced by small solute impurities.[5]

Hamilton gastight syringes, 25 μL capacity, were used to inject the solutes into the carrier gas stream. Methane was used as the inert gas tracer, to obtain the reference retention time t_0. For most of the solutes, good peaks were obtained by injecting 10−15 μL of vapor, together with a similar amount of methane. In the case of high boiling point solutes, the needle of the syringe was just wet with the liquid, to ensure infinite dilution.

To check the reproducibility of the experimental data, hexane was injected periodically during a set of runs. Solvent losses in triacetin columns were detected at 343 K and 353 K, by the systematic decrease of hexane retention time. The loss of solvent was determined by weighing the column every 4−6 h, and it was found to be proportional with time. For this reason the mass of solvent in the column was corrected assuming a linear solvent loss at each isotherm. Columns of tributyl phosphate showed no mass loss.

Results and Discussion

Table 1 contains infinite dilution activity coefficients of several solutes in tributyl phosphate at 325 K and 344 K. Two different column lengths (2 m and 1 m) were used for the measurements at 325 K. Good reproducibility was obtained, as can be inferred from the values in the table.

Li et al.[6] have published data on activity coefficients of hexane, heptane, cyclohexane, benzene, chloroform, and carbon tetrachloride in tributyl phosphate, measured at 298 K by a headspace technique. These data were extrapolated to infinite dilution, using a regular solution plus Flory's combinatorial model, together with the parameters obtained by the authors from a fitting procedure. These values have been included in Table 1; they show a good agreement with the data obtained in this work.

Table 2 gives the γ^∞ values of different solutes in triacetin at three different temperatures. The data at 343 K and 353 K were corrected for solvent loses. The values given in Table 2 are the average of the data measured in columns with different masses of stationary phase. All experimental data were reproducible within ±3%.

The temperature dependence of γ^∞ is important, to evaluate the effect of operating temperatures in solvent selectivity.

$$\left[\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right]_{P,x} = \frac{H_i^{E\infty}}{R} \tag{3}$$

For most solutes in tributyl phosphate, the changes of γ_i^∞ with temperature were small and within the range of the experimental uncertainties. No conclusion can be drawn about the sign and value of $H_i^{E\infty}$ in the reduced range of temperature studied in this work. Figure 1 shows a linear dependence of ln γ^∞ on $1/T$ for some solutes in triacetin. The partial molar excess enthalpy at infinite dilution $H_i^{E\infty}$ is clearly positive for alkanes and alcohols, which indicates a tendency toward more ideal behavior at increasing temperatures.

There is a considerable difference between the values of γ^∞ of alkanes and aromatic hydrocarbons in triacetin. This compound appears then as a potential solvent for the separation of aliphatic from aromatic hydrocarbons.

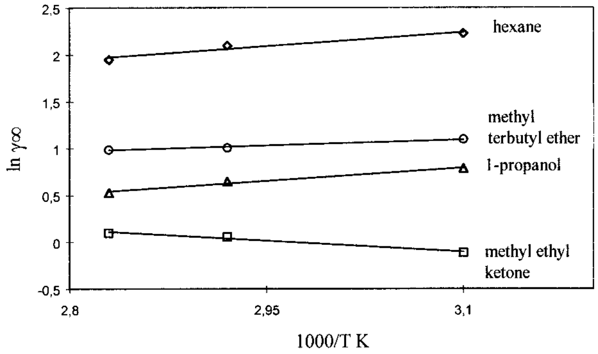

Figure 1. Temperature dependence of infinite dilution activity coefficients in triacetin.

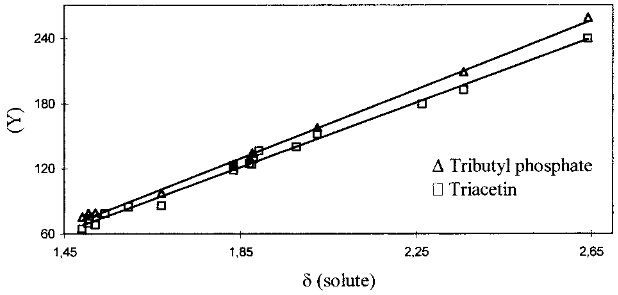

Figure 2. Residual function *Y* (eq 7) for triacetin and tributyl phosphate as a function of solute solubility parameters.

Solubility Parameters

Infinite dilution activity coefficients can be calculated by the addition of two terms, combinatorial (comb) and residual (res):

$$\ln \gamma_i^{\infty} = \ln \gamma_i^{\infty\text{comb}} + \ln \gamma_i^{\infty\text{res}} \tag{4}$$

where Flory's expression can be applied in the combinatorial contribution and the regular solution theory in the residual term.

$$\ln \gamma_i^{\infty\text{comb}} = \ln(r_i/r_s) + 1 - (r_i/r_s) \tag{5}$$

$$\ln \gamma_i^{\infty\text{res}} = (v_i/RT)(\delta_i - \delta_s)^2 \tag{6}$$

In these equations r_i/r_s represents the ratio between the solute and solvent van der Waals volumes, δ_i and δ_s are the solubility parameters, and v_i is the solute molar volume.

Equation 6 can be rearranged in terms of a residual function *Y*:

$$Y_i \equiv -\frac{\ln \gamma_i^{\infty\text{res}}}{v_i} + \frac{\delta_i^2}{RT} = (2\delta_s/RT)\delta_i - \delta_s^2/RT \tag{7}$$

This equation shows that, for a given solvent and temperature, there is a linear function between Y_i and the solute solubility parameters δ_i. From the slope of this line, the value of the solvent solubility parameter δ_s can be obtained.

The values of Y_i for each solvent were calculated as the difference between the experimental γ_i^{∞} data from Tables 1 and 2 and the corresponding $\gamma_i^{\infty\text{comb}}$ calculated by eq 5. Information on v_i, δ_i for each solute was obtained from the literature.[7] The ratios r_i/r_s in eq 5 were calculated using UNIFAC group volume parameters.[8] For tributyl phosphate, the value of $r = 10.475$ reported by Li et al.[6] was adopted.

Figure 2 shows that the data obtained in this work follow the linear dependence between Y_i and δ_i given by eq 7. From the slopes of these lines values of $\delta_s = 2.03\text{E}{+}04$ $(\text{J/m}^3)^{0.5}$ for triacetin and $\delta_s = 2.13\text{E}{+}04$ $(\text{J/m}^3)^{0.5}$ for tributyl phosphate were obtained.

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