Infinite Dilution Activity Coefficients and Solubilities of Biphenyl in Octadecane and Mineral Oil

Andrea C. Mengarelli, Susana B. Bottini, and Esteban A. Brignole*

PLAPIQUI, UNS-CONICET, 8000 Bahía Blanca, Argentina

Infinite dilution activity coefficients and solubilities of biphenyl in octadecane and in mineral oil are reported. The mineral oil is characterized by means of its molecular weight, effective molar volume, and solubility parameter. Flory's combinatorial model with a regular solution residual term is used to correlate the experimental results.

Introduction

Biphenyl is a very stable and highly toxic chemical, used extensively as a heat transfer medium. It is solid at ambient temperature, with a relatively high vapor pressure. Therefore, air treatment is required to reduce the biphenyl concentration to safe values in processing areas where biphenyl is exposed directly to the atmosphere. An absorption process has been developed to remove this contaminant from air. The absorption solvent has to be a nonpolar compound with a very low vapor pressure so as to avoid further contamination of the air. A suitable choice for this application is a mineral oil. The absorption cycle is completed with a crystallization stage to partially remove the biphenyl from the solution and to recover the oil.

The design of the separation process requires vapor-liquid and solid-liquid equilibrium data for the system biphenyl + mineral oil. The measurement of vapor and liquid compositions at equilibrium is hindered by the low concentrations of biphenyl. Besides, the high melting point of biphenyl (341.16 K) complicates the handling of vapor samples.

The conditions of vapor-liquid and solid-liquid equilibria can be expressed in terms of the activity coefficient γ_i of biphenyl in the liquid phase:

$$f_i = \gamma_i x_i f_i^\circ \tag{1}$$

In this equation f_i° represents the fugacity of pure biphenyl at the temperature of the solution. At solid-liquid equilibrium conditions, biphenyl is a subcooled liquid; in this case, f_i° can be obtained from the fugacity of pure solid biphenyl (f_i^s), using the classical thermodynamic relation

$$\ln(f_i^\circ/f_i^s) = (\Delta_{\text{fus}}H_i/R)(1/T - 1/T_{\text{fus},i}) \tag{2}$$

where $T_{\text{fus},i}$ and $\Delta_{\text{fus}}H_i$ are the temperature and enthalpy of fusion of biphenyl at its normal melting point.

The activity coefficients of biphenyl in mineral oil can be calculated from a conventional excess Gibbs free energy model, such as UNIFAC (Fredenslund et al., 1975) or regular solution theory (Hildebrand et al., 1970). Even though the nonideality of an oil + biphenyl mixture can be expected to be low, the oil is not a well-defined solvent, with a molecular weight considerably higher than that of biphenyl. Therefore, the activity coefficients will result from combinatorial as well as energetic interactions.

Experimental values of biphenyl activity coefficients can be obtained, at infinite dilution, by retention time measurements in a gas chromatograph, using the mineral oil as the column stationary phase. Additional sources of biphenyl activity coefficients, at finite concentrations in the liquid phase, are solid-liquid equilibrium measurements on biphenyl + mineral oil solutions.

Table 1. Physical Properties of the Mineral Oil

property	value
density (20 °C)	0.865 g·cm^{-3}
viscosity (40 °C)	31.0×10^{-6} $\text{m}^2\text{·s}^{-1}$
viscosity (100 °C)	5.1×10^{-6} $\text{m}^2\text{·s}^{-1}$
molecular weight	436
composition:	
aromatic carbons	3.4%
naphtenic carbons	31.8%
parafinic carbons	64.8%

The mineral oil used in the present work is classified as a turbine oil, with the general properties as given in Table 1. The average molecular weight of the oil was directly obtained from the freezing-point depression experiments (Shoemaker and Garland, 1967).

Activity coefficients at infinite dilution in mineral oil were measured for several organic solutes of different polarity, size, and shape. With these results, it was possible to characterize the solvent properties of the mineral oil, and to check the reliability of the predicting procedure. Similar measurements on the infinite dilution activity coefficients in octadecane were obtained in order to compare the mineral oil with a pure paraffinic solvent.

The use of a physical-absorption process for a solute which has a very high solubility in the solvent leads, in principle, to the requirement of very low solvent flow rates. This, in turn, leads to the use of a solvent recirculation scheme, in order to assure a good contact between the gas and liquid streams. To reduce the total solvent consumption, a multistage scheme, with recirculation, is proposed. In the present case, the solvent can also be partially regenerated by crystallization.

The separation concepts and thermodynamic modeling discussed in this work can be extended to the purification of air from other contaminants, which are solid at room temperature, but with relatively high vapor pressures.

Infinite Dilution Activity Coefficient Measurements

Infinite dilution activity coefficients of different organic solutes in octadecane and mineral oil were measured by gas-liquid chromatography (Laub and Pecsok, 1978). The specific retention volume V°_g at 273.15 K, i.e., the normalized volume of carrier gas necessary to elute solute i out of a column with a mass W_s of solvent, is calculated from the

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measured retention time (t_i) of solute i by

$$V^\circ_g = (t_i - t_a)F(273.15/T_f)((P_f - P_w^s)/P_o)J_3^2/W_s \quad (3)$$

where t_a is the dead or inert gas retention time, F is the carrier gas flow, measured at temperature T_f and pressure P_f in a soap-film meter; P_w^s is the saturated vapor pressure of water at T_f; P_o is the outlet column pressure, and J_3^2 is the James–Martin correction factor for the pressure gradient and gas compressibility inside the column (Conder and Young, 1979). Equation 4 gives, in turn, the thermodynamic relationship between the retention volume V°_g and the infinite dilution activity coefficient γ_i^∞ of solute i in solvent s.

$$\ln \gamma_i^\infty = \ln(R(273.15)/(M_s P_i^s V^\circ_g)) - (B_{ii} - v_i)P_i^s/(RT) \quad (4)$$

In this expression, the virial equation of state has been used to correct for the nonideality in the gas phase. B_{ii}, v_i, and P_i^s represent, respectively, the second virial coefficient, liquid molar volume, and vapor pressure of solute i at column temperature T, R is the universal gas constant, and M_s is the molecular weight of the solvent. Second virial coefficients and liquid molar volumes were calculated with the Hayden–O'Connell (Ried et al., 1977) and Yenny–Wood (Ried et al., 1977) correlations, respectively. The Antoine equation was used for the solute vapor pressures (Antoine coefficients from Ried et al. (1977)).

A Varian (model 3700) gas chromatograph with a FID detector and a Hewlett-Packard (model 3392) integrator were used in the measurements. The columns were immersed in a thermostatic liquid bath, placed inside the chromatograph oven, in order to assure thermal stability within ±0.1 K. The carrier gas was hydrogen, flowing at about 40 cm^3/min; a soap-film meter was used to measure the gas flow rates. Column inlet and outlet pressures were measured with a strain-gauge manometer (Aschroft, 0–60 psi) and a quartz transducer (Paroscientific), respectively. Pressure drops in the column ranged from 600 to 800 mbar. Temperatures were measured by thermistor thermometers (YSI-400). The solutes were injected into the carrier gas by using gas-tight Hamilton syringes.

The stationary phase for each column was prepared by dissolving, in chloroform, weighed amounts of solvent and inert support (Chromosorb W, 60/80 mesh), at a ratio of 3 parts of chromosorb/part of solvent. The chloroform was then evaporated from the solution, in an inert atmosphere, using a rotoevaporator (Heidolph). Stainless steel tubes, each 1/8 in. o.d. by 1 m long, were packed with about 1.5 g of each stationary phase.

In order to obtain the dead volume or reference retention time t_a, methane was always injected together with each solute. The nonretention of methane in the stationary phase was checked against the constancy of the methane retention time at different column temperatures.

The products used in the experiments were from Aldrich Chemical Co., hexane (99+%), hexene (99+%), 1,2-dichloroethane (99+%), trichloroethylene (99+%), ethylbenzene (99+%), octadecane (97%), Mallinckrodt, heptane (boiling range 4 K), Sintorgan, cyclohexane (purum grade), Raudo, benzene (purum grade), toluene (purum grade), Dorwil, chlorobenzene (purum grade).

Tables 2 and 3 contain, respectively, the infinite dilution activity coefficients of the different solutes in octadecane and in mineral oil. The uncertainties in the measured variables were estimated to be ±0.9 cm^3/min for the carrier gas flow, ±0.1 K for temperatures, ±6 mbar for the inlet pressure, ±0.1 mbar for the outlet pressure, ±1 mg for the mass of solvent in the column. Applying these limits of errors in the measured variables to the expressions obtained by differentiating eqs 3 and 4, an overall uncertainty on the order of 3% is determined for the infinite dilution activity coefficient values reported in Tables 2 and 3. Before each set of measurements, infinite dilution coefficients of hexane were routinely measured to check the apparatus operating conditions. The reproducibility of the hexane values was in accordance with the predicted experimental uncertainty.

Table 2. Infinite Dilution Activity Coefficients of Solutes in Octadecane

solute	t = 60 °C	t = 80 °C	t = 100 °C	t = 120 °C
hexane	0.90	0.91	0.97	
heptane	0.91	0.93	1.00	
hexene	0.90	0.91	0.95	
cyclohexane	0.77	0.76	0.79	
1–2-dichloroethane	1.57	1.45	1.39	
trichloroethylene	0.83	0.82	0.84	
benzene	0.91	0.90	0.89	
toluene	0.90	0.91	0.93	
ethylbenzene	0.99	0.98	0.99	
chlorobenzene	1.04	1.03	1.03	
biphenyl				1.29
naphthalene			1.41	1.19

Table 3. Infinite Dilution Activity Coefficients of Solutes in Mineral Oil

solute	t = 60 °C	t = 80 °C	t = 100 °C	t = 120 °C
hexane	1.01	1.01	1.03	1.04
heptane	1.07	1.07	1.07	1.01
hexene	1.02	1.02	0.98	0.94
cyclohexane	0.78	0.76	0.80	0.71
1–2-dichloroethane	1.38	1.27	1.17	1.07
trichloroethylene	0.77	0.76	0.78	0.73
benzene	0.86	0.86	0.88	0.75
toluene	0.87	0.87	0.83	0.78
ethylbenzene	0.97	0.94	0.93	0.91
chlorobenzene	0.96	0.92	0.90	0.85
biphenyl			1.34	1.40
naphthalene		1.19	1.13	1.02

Solid–Liquid Equilibrium Measurements

The activity coefficients of biphenyl in octadecane and in mineral oil, at solid–liquid equilibrium conditions, were determined from the measurement of the cooling curves of biphenyl + octadecane and biphenyl + oil solutions.

The experimental technique (Shoemaker and Garland, 1967) is based on the relation between the solid–liquid equilibrium conditions and the cooling curve of a given solution. A liquid mixture of known composition is cooled until a solid phase is formed. The temperature of the solution is recorded against time. A break point in the temperature vs time curve indicates the precipitation of a solid phase. The temperature at this point is the solid–liquid equilibrium temperature, and the composition of the solution gives the solubility of the solid solute in the solvent. When a pure compound or a eutectic solution is cooled, the temperature remains constant at solidification. Supercooling of the solution can occur during the experiments, due to the phenomenon of nucleation that precedes crystal formation. In this case, the freezing temperature of the solution can be obtained by extrapolating back the part of the cooling curve that follows supercooling, until it intersects the cooling curve of the original liquid solution. In the present work supercooling never exceeded 2.5 K. Each experimental data point was repeated at least three times, and the experimental freezing temperatures obtained by the extrapolation procedure described above agreed within ±0.5 K.

Table 4. Experimental and Ideal Freezing Temperatures for Biphenyl (1) + Naphtalene (2)

x_1	t_f/°C	t_f(id)/°C	x_1	t_f/°C	t_f(id)/°C
0.00	78.73	78.73	0.56	39.05	40.25
0.08	74.34	74.00	0.61	43.00	44.23
0.17	69.27	68.78	0.66	47.84	48.05
0.26	63.11	62.94	0.77	55.61	55.27
0.36	56.35	56.34	0.88	62.05	62.04
0.45	48.35	48.72	1.00	68.47	68.47
0.50	44.54	44.41			

Table 5. Solid–Liquid Equilibrium of Biphenyl (1) + Octadecane (2)

x_1	t_f/°C	γ_1	γ_2
0.000	28.10		1.00
0.155	26.45		1.03
0.225	25.97		1.08
0.246	25.66		1.08
0.252	25.62		1.09
0.266	25.42	1.46	1.09
0.292	30.71	1.52	
0.355	39.10	1.52	
0.414	44.45	1.47	
0.524	51.80	1.36	
0.622	55.60	1.24	
0.712	59.07	1.17	
0.794	61.06	1.09	
0.868	63.42	1.04	
0.937	65.62	1.01	
1.000	68.47	1.00	

Table 6. Solid–Liquid Equilibrium of the Biphenyl (1) + Mineral Oil (2) System

x_1	t_f/°C	γ_1	x_1	t_f/°C	γ_1
0.176	2.29	1.18	0.582	50.73	1.20
0.197	6.99	1.21	0.604	51.32	1.17
0.219	11.79	1.24	0.624	53.13	1.18
0.239	15.04	1.24	0.654	54.63	1.16
0.269	20.40	1.27	0.739	58.33	1.11
0.297	24.09	1.27	0.809	61.23	1.07
0.324	28.33	1.29	0.840	62.73	1.06
0.350	31.78	1.30	0.868	63.03	1.04
0.383	35.29	1.29	0.895	64.37	1.03
0.414	38.62	1.29	0.919	65.19	1.02
0.458	41.91	1.26	0.962	66.87	1.01
0.485	43.63	1.23	0.982	67.58	1.00
0.511	46.13	1.29	1.000	68.47	1.00
0.548	48.52	1.22			

The experimental apparatus consists of an inner glass tube of 50 cm^3 capacity, which contains the solution to be studied, surrounded by an insulating material and an outer glass jacket. This assembly is immersed in a thermostatic liquid bath, whose temperature is set at about 293.15 K below the expected freezing temperature of the solution. The solution to be studied is prepared by weighing the materials to ±0.1 mg on an analytical balance (Mettler, AE163). The temperature of the solution is measured with a 100 Pt resistance thermometer, connected to a digital indicator (Systemteknik AB, S1220, resolution ±0.001 K) and a recorder (Varian, model 9176). Stirring of the solution is achieved by the vertical movement of a coiled wire, driven by a small electrical motor.

The experimental apparatus and technique were first checked by measuring the cooling curves of biphenyl + naphthalene solutions. As expected, this system showed an ideal behavior. Table 4 contains the measured freezing temperatures and the ideal values calculated from eq 5 with $\gamma_i = 1$. The eutectic was measured at 312.15 K and 0.555 mole fraction biphenyl.

Tables 5 and 6 give, respectively, the results of the solid–liquid equilibrium measurements for the systems biphenyl + octadecane and biphenyl + mineral oil. The activity coefficient values reported in these tables were obtained from the thermodynamic relation

$$\gamma_i = (1/x_i)\exp[(1/T - 1/T_{\mathrm{fus},i})\Delta_{\mathrm{fus}}H_i/R] \qquad (5)$$

where T is the freezing temperature of a solution of composition x_i, $T_{\mathrm{fus},i} = 341.63$ K, and $\Delta_{\mathrm{fus}}H_i = 18\,577$ J/mol for pure biphenyl (Daubert and Danner, 1991).

The molecular weight of the mineral oil was also determined from the biphenyl + mineral oil solid–liquid equilibrium data, by extrapolating the molecular weights calculated from each experimental data point to a freezing-point depression equal to zero (Shoemaker and Garland, 1967). A molecular weight of 436 was obtained.

Thermodynamic Modeling

The infinite dilution activity coefficient data are useful to characterize the mineral oil as a solvent for organic solutes. The characterization of the oil can be made by means of a group contribution method, considering the fraction of paraffinic, naphthenic, and aromatic hydrocarbons given in Table 1. A different approach used was to apply a predictive thermodynamic model, such as Flory's model with a regular solution residual contribution (Hildebrand et al., 1970). In this case two parameters are required to characterize the oil: the solubility parameter and a size parameter.

The differences in molecular size between the solvents (mineral oil and octadecane) and most of the solutes studied in this work make the entropic contribution to the total value of the activity coefficient significant. The residual contribution can be correlated with the UNIFAC local composition approach or with the regular solution theory. The application of regular solution theory appears to be convenient in the present case, considering that the data are at infinite dilution. Moreover, most of the solutes present moderate deviations from ideality in mixtures with mineral oil and octadecane.

Using Flory's model with a regular solution residual contribution, the activity coefficient of component i (γ_i) is calculated by

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{comb}} + \ln \gamma_i^{\mathrm{res}} \qquad (6)$$

where

$$\ln \gamma_i^{\mathrm{comb}} = \ln(\phi_i/x_i) + 1 - (\phi_i/x_i) \qquad (7)$$

and

$$\ln \gamma_i^{\mathrm{res}} = (v_i/RT)(\delta_i - \delta_j)^2\phi_i \qquad (8)$$

The volume fraction ϕ_i is defined as

$$\phi_i = v_i^p x_i / \sum v_i^p x_i \qquad (9)$$

In Flory's original model the exponent $p = 1$. Kikik et al. (1980) have proposed to use $p = 2/3$, on the basis of their good results for hydrocarbon mixtures.

Eqs 6–9 were used to calculate the activity coefficients of different solutes in octadecane. The mean differences between the calculated and the experimental data from Table 2 were 8% when Flory's original volume fraction definition was applied and 2% with Kikik's 2/3 exponent. In these calculations, the values of the volume v_i and solubility parameter δ_i for the different compounds were taken from the literature (Daubert and Danner, 1991; Edmister and Lee, 1984). For octadecane those values were 329 cm^3/mol and 16.51 (J/cm^3)$^{1/2}$, respectively. A good fit of the experimental data (within the experimental uncertainties) is then achieved by using Flory's model with a regular solution residual contribution and a 2/3 exponent in the definition of the volume fraction.

In order to apply this model to represent the activity coefficients in mineral oil, it is necessary to know the values of the solubility parameter and the effective molar volume of the mineral oil. The experimental data from Table 3 were used to calculate these parameters. A Marquard minimization procedure was applied, together with the following objective function:

$$F(v_{\mathrm{oil}},\delta_{\mathrm{oil}}) = \sum(\gamma_i^{\mathrm{exptl}} - \gamma_i^{\mathrm{calcd}})^2 \qquad (10)$$

Values of 16.73 $(\mathrm{J/cm^3})^{1/2}$ for the solubility parameter and 306.8 $\mathrm{cm^3/mol}$ for the effective molar volume were obtained, with a mean quadratic deviation between calculated and experimental infinite dilution activity coefficients of 0.8%.

The measured density of the mineral oil was 0.865 $\mathrm{g/cm^3}$ at room temperature, which corresponds to a molar volume of 504 $\mathrm{cm^3/mol}$. The effective molar volume of the mineral oil (306.8 $\mathrm{cm^3/mol}$) is similar in magnitude to the molar volume of octadecane (325 $\mathrm{cm^3/mol}$). This means that, even though the mineral oil is made up of components with chain lengths longer than that of octadecane, molecular branching and bending result in a molecular configuration similar to that of octadecane.

With these results for the characterization of the mineral oil, solid–liquid equilibrium predictions for the biphenyl + mineral oil system were carried out throughout the concentration range. Figure 1 shows good agreement between the calculated and the experimental data, with a mean quadratic deviation of 0.53%. Similar predictions for the biphenyl + octadecane system gave a mean quadratic deviation of 1.5%.

With the mineral oil characterized through its effective molar volume and its solubility parameter, Flory's model with a regular solution residual contribution can be applied to predict the vapor–liquid and solid–liquid equilibria of solutions of the mineral oil with nonpolar, polarizable, and slightly polar compounds.

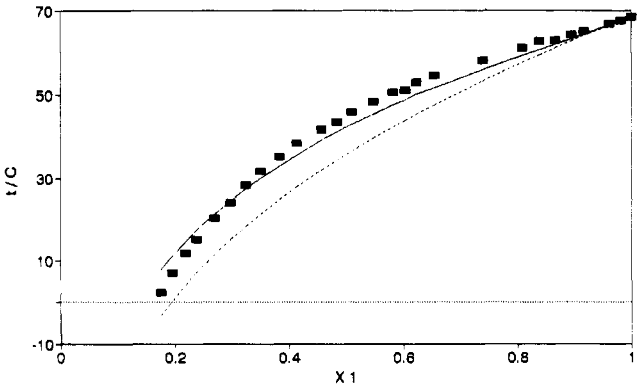

Figure 1. Solid–liquid equilibrium for biphenyl (1) + mineral oil (2): (■) experimental data, (···) ideal curve, (—) predicted curve.

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