Excess Free Energies of the Systems Carbon Tetrachloride–Pyridine and Pyridine-Tetrachloroethylene

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The excess free energies of the systems carbon tetrachloride–pyridine and pyridine-tetrachloroethylene have been calculated from reliable vapor-liquid equilibrium data at 50° C. The data were obtained with a modified Gillespie equilibrium still and proved consistent by a thermodynamic evaluation.

IN QUANTITATIVE THERMODYNAMIC and statistical treatment of solutions the properties of a real solution are usually compared with those of an ideal one. The most convenient way is to use the excess property, which is defined by the equation

$$\Delta \overline{Z}_i^E = \overline{Z}_i - \overline{Z}_i^* \tag{1}$$

Thus the excess free energy can be written

$$\Delta \overline{G}_i^E = \overline{G}_i - \overline{G}_i^* \tag{2}$$

and for one mole of a solution

$$\Delta G^E = \sum_i x_i \Delta \overline{G}_i^E = RT \sum_i (x_i \ln \gamma_i) \tag{3}$$

The greater the excess free energy, the more pronounced the difference in behavior between a real and an ideal solution. When molecules of two substances are nonpolar and have the same symmetry, shape, and size, it is expected that they will form an ideal solution. Both systems treated here are nonideal solutions. As the molecules of carbon tetrachloride and tetrachloroethylene are nonpolar and have approximately the same size and symmetry, one could expect the difference in the excess free energies of the systems carbon tetrachloride–pyridine (CT-P) and pyridine-tetrachloroethylene (P-TCE) at the same concentration of pyridine to be mostly due to the interaction between the dipole moment of pyridine and the double bond of tetrachloroethylene. This approximation requires that the factors upon which the nonideality of a solution depends be separable; this is to a certain degree unjustified, but seems to be very helpful in the statistical treatment of solutions.

EXPERIMENTAL

Chemicals. Pyridine and tetrachloroethylene were purified by a method described earlier (*2*). Fisher spectroanalyzed carbon tetrachloride was twice distilled and dried as usual. The measured density at 25° C. (1.58448 grams per cc.) and the normal boiling point (76.73° C.) were in good agreement with the values given in the literature (76.7–76.75° C., 1.58452) (*10*). At atmospheric pressure, the boiling point and the condensation temperature measured with a Beckman thermometer in a modified Swietoslavski differential ebulliometer (*4*) differed by only 0.002° C. This indicated that the sample did not contain sufficient impurities of different volatilities to have a significant effect on the boiling point measurement.

Apparatus and Procedure. The vapor-liquid equilibrium data were obtained as before with a modified Gillespie circulation equilibrium still (*4, 10*). To avoid superheating of the standard liquid (water) in the ebulliometer and to get more accurate readings for the pressure, the inside walls of the boiling flask of the ebulliometer were effectively activated by ground glass of particle size from 0.25 to 0.30 mm. (50-mesh). The vapor pressure of water as a function of temperature is known very accurately, so that the pressure of the system was measured with high accuracy as well (±0.05 mm. of Hg) (*2*). The glass particles must be fused to the walls in such a manner that they remain sharp and active. Because of the hygroscopic nature of the pyridine, all measurements were made in a dry nitrogen atmosphere. Even under these conditions, solution CT-P turned slightly yellow and solution P-TCE turned slightly pink. This indicates that both chlorohydrocarbons decompose partially in the presence of the pyridine base. However, gas-liquid chromatography studies revealed that the decomposition is very slight and was ignored.

The temperature was measured with a mercury thermometer calibrated by the National Bureau of Standards. The uncertainty in the temperature reading was ±0.015° C.

Vapor and liquid equilibrium samples were analyzed by density measurements at 25° ± 0.02° C., using a standard pycnometric technique. To obtain more accurate results

Table I. Densities of the Systems Pyridine–Tetrachloroethylene and Carbon Tetrachloride–Pyridine at 25° C.

Pyridine (1)	Tetrachloro-ethylene (2)	Carbon Tetrachloride (1)	Pyridine (2)
x_1	d	x_1	d
0.0233	1.6021	0.0367	1.0058
0.0563	1.5849	0.0878	1.0435
0.0906	1.5668	0.1427	1.0827
0.1738	1.5219	0.2527	1.1587
0.1851	1.5159	0.3528	1.2245
0.2065	1.5040	0.4724	1.2992
0.2883	1.4581	0.6082	1.3791
0.3880	1.3999	0.6741	1.4161
0.4670	1.3527	0.6995	1.4301
0.4764	1.3470	0.7131	1.4375
0.6460	1.2379	0.8695	1.5194
0.7283	1.1817	0.9419	1.5555
0.8740	1.0762	0.9483	1.5586
0.9276	1.0352	0.9551	1.5618
0.9827	0.9920	0.9671	1.5678

for the composition of the unknown sample, ΔV_{mix} was calculated from the experimental density-composition data as a function of the composition using the relationship

$$\frac{\Delta V_{\text{mix}}}{x_1x_2} = a + b(x_1 - x_2) + c(x_1 - x_2)^2 + \ldots\ldots \tag{4}$$

where

$$\Delta V_{\text{mix}} = \frac{x_1M_1 + x_2M_2}{d} - \frac{x_1M_1}{d_1} - \frac{x_2M_2}{d_2} \tag{5}$$

The density of the unknown solution was measured and its composition was found using a computer program which solved both equations simultaneously. The values of the constants of Equation 4, for both systems, calculated by the method of least squares, CT − P, a = −2.010, b = 0.858, c = 0.619, and σ = ±0.224; and P-TCE, a = 0.442, b = −0.689, c = 0.697, and σ = ±0.239 (the units are cubic centimeters per mole). A precision in the density measurements of ±0.0001 gram per cc. would give a precision in the determination of the composition of better than 0.02 mole %. However, the magnitude of the standard deviations reduces the precision in both cases to ±0.05 mole % (Table I).

RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium data are presented in Table II and Figure 1.

For the thermodynamic correlation of both systems, two types of equation have been used: the Margules fourth-order equation (*4*) in the form

$$\log \frac{\gamma_1}{\gamma_2} = x_2^2A_{12} - x_1^2A_{21} - 2x_1x_2[A_{12} - A_{21} + (x_2 - x_1)D] \tag{6}$$

and the series expansion of the relative volatility

$$\alpha_{12} = \frac{y_1x_2}{y_2x_1} = \frac{\gamma_1P_1^\circ C_2}{\gamma_2P_2^\circ C_1} \tag{7}$$

Table II. Vapor-Liquid Equilibrium in the Binary Systems at 50° C.

x_1	y_1	P, Mm. of Hg	C_1	C_2	Deviation in Vapor-Phase Composition	
					Margules	α-Series
Carbon Tetrachloride (1)–Pyridine (2)						
0.0141	0.0841	78.16	1.0155	0.9994	0.0018	0.0008
0.0898	0.3733	106.57	1.0136	0.9970	0.0000	−0.0005
0.1370	0.4808	122.31	1.0126	0.9957	−0.0021	−0.0004
0.1804	0.5554	136.43	1.0116	0.9945	−0.0024	−0.0008
0.2347	0.6283	152.36	1.0105	0.9931	−0.0013	0.0013
0.3855	0.7528	193.54	1.0078	0.9897	−0.0030	−0.0012
0.4953	0.8134	219.25	1.0061	0.9875	−0.0010	−0.0005
0.5705	0.8472	243.04	1.0051	0.9863	0.0007	0.0005
0.6418	0.8739	248.50	1.0042	0.9851	0.0007	0.0008
0.6996	0.8942	258.82	1.0035	0.9842	0.0007	−0.0006
0.7013	0.8948	259.42	1.0034	0.9842	0.0008	−0.0005
0.7547	0.9138	269.18	1.0028	0.9833	0.0023	0.0003
0.8331	0.9396	283.34	1.0019	0.9822	0.0012	−0.0003
0.8754	0.9538	291.02	1.0013	0.9815	0.0008	−0.0003
0.8982	0.9618	294.38	1.0011	0.9812	0.0007	−0.0002
0.9265	0.9721	299.08	1.0008	0.9809	0.0007	0.0001
0.9281	0.9729	300.63	1.0007	0.9807	0.0010	0.0003
0.9800	0.9922	308.45	1.0002	0.9801	0.0004	0.0002
				Mean	0.0012	0.0006
Pyridine (1)–Tetrachloroethylene (2)						
0.0466	0.1047	66.06	1.0005	0.9996	0.0017	0.0012
0.1349	0.2425	72.57	0.9999	0.9989	0.0005	−0.0006
0.2592	0.3657	77.05	0.9996	0.9985	0.0003	−0.0004
0.3323	0.4204	79.07	0.9994	0.9983	0.0005	0.0001
0.3727	0.4479	79.92	0.9993	0.9982	0.0005	0.0003
0.4285	0.4845	80.57	0.9993	0.9981	0.0000	0.0000
0.4612	0.5043	80.97	0.9993	0.9981	0.0008	0.0009
0.5225	0.5442	81.32	0.9992	0.9980	−0.0007	−0.0006
0.5576	0.5662	81.41	0.9992	0.9980	−0.0005	−0.0004
0.5773	0.5786	81.45	0.9992	0.9980	−0.0001	−0.0002
0.5801	0.5801	81.47	0.9992	0.9980	0.0002	0.0002
0.5957	0.5902	81.40	0.9992	0.9980	0.0003	0.0002
0.6930	0.6590	81.20	0.9992	0.9981	−0.0003	−0.0008
0.7063	0.6677	81.02	0.9992	0.9981	0.0011	0.0006
0.8564	0.8027	79.00	0.9994	0.9983	0.0014	0.0006
0.9246	0.8855	76.11	0.9996	0.9986	0.0000	−0.0006
				Mean	0.0006	0.0005

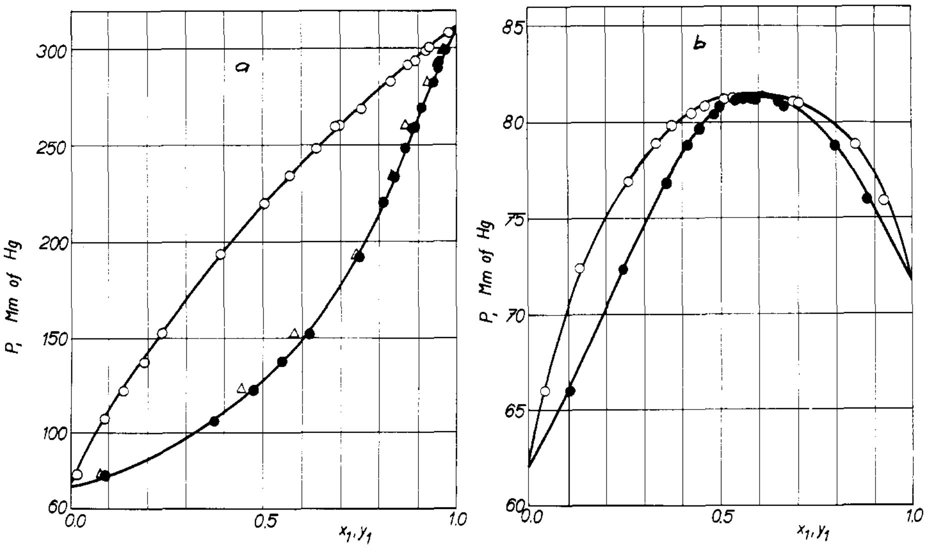

Figure 1. Vapor-liquid equilibrium of the binary systems at 50° C.

a. Carbon tetrachloride (1)–pyridine (2) Δ data calculated from Equation 14

b. Pyridine (1)–tetrachloroethylene (2)

which can be written

$$\log \frac{\gamma_1}{\gamma_2} = \log \alpha_{12} - \log \frac{P_1^\circ}{P_2^\circ} + \log \frac{C_1}{C_2} =$$

$$\log \left[\frac{1 + a_{12}x_2 + a_{122}x_2^2}{1 + a_{21}x_1 + a_{211}x_1^2} \right] - \log \frac{P_1^\circ}{P_2^\circ} + \log \frac{C_1}{C_2} \quad (8)$$

For system CT-P the relative volatility as a function of the composition can be presented by a linear relationship

$$\alpha_{12} = A + Bx_1 \quad (9)$$

In calculating the activity coefficients the authors assumed that the vapor phase is an ideal solution of nonideal vapors (coefficient Δ_{12}, defined by the equation $\Delta_{12} = 2B_{12} - B_{11} - B_{22}$, is equal to zero), and the following equation was used

$$\gamma_i = \frac{y_i P}{x_i P_i^\circ} C_i \quad (10)$$

where

$$C_i = \exp\left[\frac{(P - P_i^\circ)(B_{ii} - V_{il}^\circ)}{RT} \right] \quad (11)$$

All the data necessary to calculate the activity coefficients are summarized in Tables II and III (*3, 5, 10*). The virial coefficients of the pure components were calculated from Pitzer's equation (*6*).

The authors discovered that for system P-TCE the ratio of the two exponents, C_1/C_2, is very close to unity at all concentrations (as is evident from Table II) and log (C_1/C_2) can therefore be neglected. Nevertheless, for system CT-P this ratio is different from unity and should be considered in the calculation. The values of γ_1 and γ_2 calculated from Equation 10 for both systems were inserted into Equations 6, 7, 8, and 9, and the constants were evaluated by the method of least squares. All the constants are given in Table IV.

The vapor-phase composition was then calculated using the relation

$$Fy_1 = \frac{\left(\frac{\gamma_1 P_1^\circ C_2}{\gamma_2 P_2^\circ C_1}\right) x_1}{1 + \left(\frac{\gamma_1 P_1^\circ C_2}{\gamma_2 P_2^\circ C_1} - 1\right) x_1} \quad (12)$$

Table III. Virial Coefficients, Vapor Pressures, and Molar Volumes of Pure Substances at 50° C.

	P_i°, Mm. Hg	B_{ii}, Ml./Mole	V_i°, Ml./Mole
Carbon tetrachloride	312.20	-1230	100.15
Pyridine	71.88	-1626	83.13
Tetrachloroethylene	61.91	-1910	105.46

Table IV. Constants of Margules Equation and Series Expansion of Relative Volatility at 50° C.

Carbon Tetrachloride–Pyridine

A_{12}	A_{21}	D	A	B
0.1691	0.2451	0.0008	6.4054	-3.9369

Pyridine–Tetrachloroethylene

A_{12}	A_{21}	D	a_{12}	a_{122}	a_{21}	a_{211}
0.3623	0.3067	0.0235	1.0876	0.5766	1.2480	-0.4951

Deviations in the calculated vapor-phase composition presented in Table II indicate that both the Margules equation and the series expansion of the relative volatility correlate the experimental data very well. The linear relationship for the relative volatility as a function of the composition for system CT-P fits the data very well. The constant D of the Margules equation for the same system is negligibly small.

The thermodynamic consistency of the experimental data was proved by the method given by Rowlinson (*9*)

$$\int_0^1 \ln \left(\alpha_{12} \frac{P_2^\circ}{P_1^\circ} \frac{C_1}{C_2}\right) dx_1 = \frac{(P_2^\circ - P_1^\circ)(V_{1l}^\circ + V_{2l}^\circ - B_{11} - B_{22})}{2RT} \quad (13)$$

Because of the small difference in the vapor pressures of pyridine and tetrachloroethylene, the right-hand side of Equation 13 for this system is negligibly small. This is not exactly the case with system CT-P; nevertheless, even for the latter system, the value of the right-hand side of Equation 13 can be neglected (−0.018). Thus, Equation 13 reduces to the Redlich-Kister consistency test method (*7, 8*). This method requires that the net area of the graph of ln $[\alpha_{12} (P_2^\circ C_1)/(P_1^\circ C_2)]$ *vs.* x_1 be equal to zero. This requirement is met in Figure 2 for both systems. The ratio of the area above and below the zero line is 0.961 for system P-TCE and 0.942 for system CT-P.

From the calculated activity coefficients of both systems, the excess free energies were found using Equation 3

$$\Delta G^E = x_1 RT \ln \gamma_1 + x_2 RT \ln \gamma_2$$

where index 1 denotes the lower boiling constituents: carbon tetrachloride in the system with pyridine and pyridine in the solution with tetrachloroethylene. The calculated excess free energies as a function of composition are plotted in Figure 3, *a* and *b*. Curve *c* gives the difference in the excess free energies of both systems at the same temperature and concentration of pyridine. The molecules of carbon tetrachloride and tetrachloroethylene are nonpolar (zero dipole moments), and have approximately the same size [$V^\circ_{CCl_4}$ = 100.15 cc. per mole; $V^\circ_{C_2Cl_4}$ = 105.46 cc. per mole; $V^\circ_{pyridine}$ = 83.15 cc. per mole; ($V^\circ_{CCl_4}/V^\circ_{pyridine}$) = 1.20) and ($V^\circ_{C_2Cl_4}/V^\circ_{pyridine}$) = 1.27], and roughly the same symmetry (both molecules are symmetrical, although CCl_4

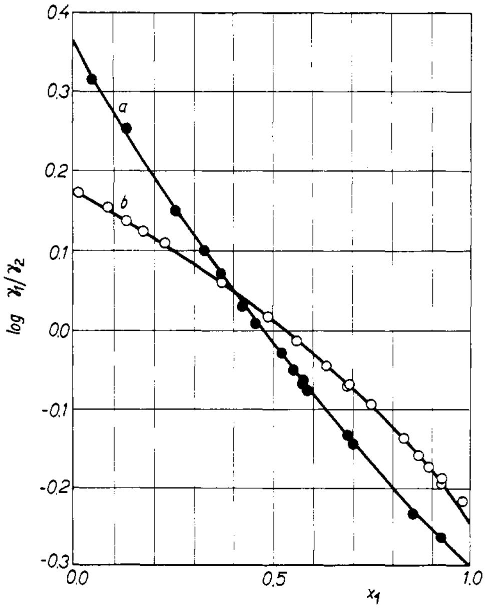

Figure 2. Thermodynamic consistency test

a. System pyridine (1)–tetrachloroethylene (2)

b. System carbon tetrachloride (1)–pyridine (2)

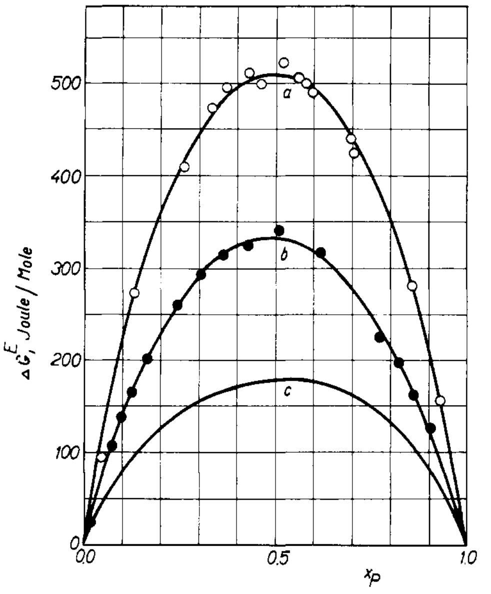

Figure 3. Excess free energies as a function of composition at 50° C.

a. System pyridine (1)–tetrachloroethylene (2)

b. System carbon tetrachloride (1)–pyridine (2)

c. Difference $(\Delta G^E)_a - (\Delta G^E)_b$ in excess free energies in both systems

has a point symmetry, while C_2Cl_4 has a plane symmetry). Thus, if the approximation on separability of the different factors affecting the nonideal behavior of a solution were justified, curve *c* would give the excess free energy resulting from the dipole–double bond interaction. More data will be necessary to discover to what extent this approximation is justified.

In conclusion, the properties of system CT-P can be well estimated from the properties of the pure constituents. The equation proposed by Erdos (*1*)

$$A_{ik} = \frac{1}{2.303}\left[(U_c)_i^{1/2} - ([P]_i/[P_k])^{2/3}(U_c)_k^{1/2}\right] \qquad (14)$$

for calculating the constants of the Van Laar equation (A_{12} and A_{21}) gives satisfactory results for the vapor-liquid equilibrium in system CT-P ($A_{12} = 0.133$ and $A_{21} = 0.124$), as is evident from Figure 1, *a*. There is, however, very poor agreement for the other system. The system pyridine-tetrachloroethylene also forms an azeotrope ($x_1 = 0.5801$ and $P = 81.36$ mm. of Hg). Apparently, the thermal agitation in the system carbon tetrachloride–pyridine is able to overcome any tendency toward molecular orientation and combination, so that this system will probably behave like a regular solution. Preliminary calculations support this fact.

NOMENCLATURE

$a, b, c, a_{12}, a_{21}, a_{122}, a_{211}, A, B, A_{12}, A_{21}, D, A_{ik}, A_{ki}$ = constants
B_{ii} = virial coefficient of pure component *i*
B_{12} = interaction virial coefficient
C_i = correction term for the vapor phase
d_i = density of pure component *i*
d = density of the solution
$\overline{G}_i$ = partial molal free energy of component *i*
$\overline{G}_i^*$ = partial molal free energy of component *i* in an ideal solution
$\Delta\overline{G}_i^E$ = partial molal excess free energy of component *i*
ΔG^E = molal excess free energy
M_i = molecular weight of component *i*
$\overline{Z}_i$ = a general partial molal quantity of component *i*
$\overline{Z}_i^*$ = partial molal quantity of component *i* in an ideal solution
$\Delta\overline{Z}_i^E$ = partial molal excess quantity of component *i*
P_i° = vapor pressure of pure component *i*
P = total pressure of the system
$[P]_i, [P]_k$ = parachors of components *i* and *k*
σT = temperature, absolute
$(U_c)_i, (U_c)_k$ = cohesion energies of components *i* and *k*
V_{il}° = molar volume of pure component *i* in the liquid phase
ΔV_{mix} = change in volume due to mixing
x_i = mole fraction of component *i* in the liquid phase
y_i = mole fraction of component *i* in the vapor phase

Greek Letters

α_{12} = relative volatility of the binary system 1-2
γ_i = activity coefficient of component *i* in the liquid phase (standard state is pure component at the temperature and pressure of the system)
σ = standard deviation

LITERATURE CITED

(1) Erdos, E., *Collection Czechoslov. Chem. Commun.* **21**, 1528 (1956).
(2) Fried, V., Gallant, P., Schneier, G. B., J. Chem. Eng. Data **12**, 504 (1967).
(3) Fried, V., Schneier, G.B., Gallant, P., Brooklyn College of the City University of New York, Brooklyn, N.Y., unpublished data, 1967.
(4) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor-Liquid Equilibrium," pp. 232, 272, 68, Pergamon Press, London, 1958.
(5) Herington, E.F., Martin, J.F., *Trans. Faraday Soc.* **49**, 154 (1953).
(6) Pitzer, K.S., Curl, R.F., *J. Am. Chem. Soc.* **79**, 2369 (1957).
(7) Redlich, O., Kister, A.T., *Ind. Eng. Chem.* **40**, 345 (1948).
(8) Redlich, O., Kister, A.T., Turnquist, C.E., *Chem. Eng. Progr. Symp. Ser.* **48**, No. 2, 49 (1952).
(9) Rowlinson, J.S., "Liquids and Liquid Mixtures," pp. 132–7, Butterworths, London, 1959.
(10) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

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