of disodium 5'-inosinate increases, resulting in a decrease of the solubility of the other two inorganic salts (sodium chloride and trisodium phosphate), whereas the solubility of 5'-inosinate is suppressed by the high solubility of the inorganic salts in the lower pH region (pH 2.0–9.5).

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Vapor-Liquid Equilibria in System Carbon Tetrachloride-Acetic Acid

Jaime Wisniak[1] **and Abraham Tamir**
Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva, Israel

Vapor-liquid equilibrium data are determined for the system carbon tetrachloride–acetic acid at 760 and 417 mm Hg. The system presents strong positive deviations from the ideal solution and at 76.17°C and 760 mm Hg exhibits an azeotrope with 94.0 mol % carbon tetrachloride. The experimental results are thermodynamically consistent only when association effects are taken into account.

The association in a phase is usually described quantitatively by the proper equilibrium constant, assuming no interaction between the different chemical species present. The experimental evidence indicates that association increases with dilution and that the main species present are the monomer and dimer (*1*), although Ritter and Simons (*12*) claim that the tetramer is also significant. The system acetic acid–carbon tetrachloride provides a good example of an associating substance mixed with a nonpolar solvent that affects the dimerization phenomena.

The general problem of association has been thermodynamically analyzed by Marek and Standart (*6, 7*), Sebastiani and Lacquaniti (*13*), and Ratkovics (*11*) by different approaches. Very few data are available on the vapor-liquid equilibrium data for the system examined. Miksch et al. (*8*) and Ratkovics (*11*) measured the total vapor pressure of acetic acid–carbon tetrachloride mixtures at 20°, 32.28°, and 40°C and reported data at 740 mm without indicating the values of the equilibrium temperatures and the activity coefficients. Houghton (*3*) studied the variation in acetic acid composition of the azeotrope and found that it dropped from 1.54 wt % at 760 mm and 76°C to 1.00 wt % at 530 mm and 64.6°C. Kenney (*4*) determined the total pressure of the binary at 25°C.

It is our purpose to provide complete vapor-liquid equilibrium data for the system acetic acid–carbon tetrachloride and to analyze the effect of association and dilution of the thermodynamic consistency of the data obtained.

Experimental

Purity of materials. Analytical-grade reagents purchased from Merck and Frutarom were employed without further purification after gas chromatographic analysis failed to show any significant impurities. Physical properties of the pure compounds appear in Table I.

Apparatus and procedure. An all-glass modified Dvorak and Boublik recirculation still (*2*) was used in the equilibrium determinations. The original apparatus was further modified after pressure equalization problems were encountered when working at temperatures above 90°C. Recirculation of the condensed vapor phase was substantially improved by providing a connection between the entrance to the vapor condenser and the condensed vapor reservoir. A vacuum system controlled by a cartesian manostat connected the vapor condenser with a Swietoslawski ebulliometer and allowed total pressure regulation. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebulliometer. Temperatures were measured with a Hewlett-Packard quartz thermometer, Model 2801A, with an accuracy of ±0.005°C, so that the accuracy of the pressure measurements was better than 0.1 mm Hg. Several 1-ml samples were taken during each run until no significant changes in the refractive index and temperature were detected. The time required for reaching equilibrium varied between 2 hr for low-temperature determinations, to 4 hr for high-temperature levels.

Analyses of the samples were made at 25°C with a Bausch & Lomb Abbe-3L precision refractometer which gave direct readings to four significant figures and estimated values reproducibly to the nearest 0.00025. The calibration data appear in Table II. These data could be represented by two straight lines with slopes dn/dx 0.0990 in the range $0 \leq x_1 \leq 0.29$ and 0.0841 in the range $0.29 \leq x_1 \leq 1.0$. The accuracy of the concentration data can thus be estimated to be at least 0.003 concentration units.

Table I. Physical Constants of Compounds at 20°C

Compound	Density	Refractive index
Carbon tetrachloride	1.5940	1.4600
	1.5940 (*15*)	1.4601 (*15*)
Acetic acid	1.0493	1.3717
	1.0492 (*15*)	1.3716 (*15*)

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[1] To whom correspondence should be addressed.

Table II. Refractive Index at 20°C of Mixtures of Carbon Tetrachloride–Acetic Acid

x_1	n	x_1	n
0.000	1.3717	0.288	1.4024
0.025	1.3750	0.300	1.4031
0.027	1.3754	0.350	1.4080
0.051	1.3775	0.361	1.4090
0.079	1.3805	0.450	1.4186
0.084	1.3811	0.500	1.4240
0.100	1.3836	0.520	1.4254
0.125	1.3856	0.591	1.4295
0.150	1.3890	0.700	1.4385
0.185	1.3919	0.800	1.4463
0.200	1.3932	0.826	1.4477
0.225	1.3964	0.900	1.4535
0.250	1.3980	0.950	1.4569
		1.000	1.4600

Table III. Experimental Vapor-Liquid Equilibrium Data

Press, mm Hg	Temp, °C	x_1	y_1	γ_1	γ_2
760	111.86	0.015	0.145	5.43071	0.99269
	109.13	0.025	0.195	4.57526	1.00396
	104.85	0.045	0.300	4.12463	0.99195
	101.41	0.055	0.340	4.11358	1.02322
	97.81	0.080	0.430	3.75743	1.00742
	94.28	0.100	0.470	3.55480	1.04556
	91.28	0.125	0.520	3.33856	1.06173
	90.40	0.140	0.540	3.14153	1.06642
	88.18	0.170	0.580	2.90293	1.08332
	86.27	0.200	0.610	2.70304	1.10933
	84.32	0.265	0.670	2.30225	1.12253
	83.25	0.290	0.690	2.21483	1.13937
	82.45	0.320	0.720	2.11368	1.13168
	79.65	0.430	0.765	1.78022	1.27731
	78.00	0.585	0.805	1.42119	1.61409
	77.15	0.725	0.860	1.22635	2.01948
	77.05	0.760	0.860	1.17349	2.31886
	76.30	0.870	0.905	1.08269	3.42386
	76.25	0.895	0.920	1.06491	3.81360
	76.22	0.910	0.925	1.05188	4.27615
	76.24	0.920	0.935	1.04686	4.39475
	76.18	0.935	0.945	1.03896	4.87157
	76.19	0.940	0.935	1.02617	5.86643
	76.20	0.945	0.940	1.02387	6.08222
	76.43	0.985	0.980	1.00621	8.68733
417	93.90	0.010	0.120	6.12074	1.01390
	80.30	0.055	0.405	4.75239	1.01169
	77.65	0.075	0.455	4.13395	1.02104
	70.65	0.145	0.590	3.22050	1.04086
	68.40	0.200	0.635	2.64136	1.07708
	65.80	0.250	0.685	2.42123	1.10027
	65.90	0.280	0.690	2.16461	1.13216
	64.70	0.320	0.710	2.00840	1.17722
	62.65	0.380	0.380	1.89215	1.19593
	62.85	0.395	0.745	1.78569	1.19593
	62.85	0.395	0.745	1.78569	1.26736
	61.95	0.420	0.780	1.78172	1.22920
	61.40	0.470	0.800	1.64781	1.28346
	61.20	0.500	0.825	1.58905	1.25969
	60.10	0.540	0.830	1.53373	1.37680
	59.85	0.645	0.832	1.29708	1.78064
	59.70	0.650	0.835	1.29661	1.79221
	59.60	0.660	0.840	1.31306	1.83791
	59.10	0.765	0.870	1.15290	2.34306
	59.00	0.815	0.860	1.07844	3.11797
	58.60	0.905	0.920	1.02535	4.38066
	58.50	0.920	0.935	1.02207	4.59942
	58.40	0.960	0.960	0.99892	6.84278
	58.60	0.975	0.965	0.97997	10.13589

Results

Constant-pressure equilibria determinations were made at 760 and 417 mm Hg, and the experimental results appear in Table III. At 760 mm and 76.17°C the system presented a minimum boiling-point azeotrope that contained 94.0 mol % carbon tetrachloride. When the pressure was lowered to 417 mm, the azeotrope became richer in the volatile component, but its properties could not be accurately determined because of the extreme flatness of the equilibrium curve.

Preliminary calculations showed that activity coefficients calculated without taking into account the association effects were thermodynamically inconsistent. Results were then correlated by using the association model and equations developed by Marek and Standart (*6*, *7*) that take into consideration the dimerization constant but neglect the effect of dilution on it. The corresponding results appear in Table III. Activity coefficients at 760 mm Hg are shown in Figure 1.

The physical properties used were as follows: vapor pressure of carbon tetrachloride (*14*):

$$\log p_1^\circ = 6.9339 - \frac{1242.43}{t + 230.1}$$

vapor pressure of acetic acid (*7*):

$$\log p_2^\circ = 14.39756 - \frac{9399.66}{t + 698.09}$$

dimerization constant (*5*):

$$-\log K_2 = 10.4205 - \frac{3166}{t + 273.15}$$

Area tests for each individual activity coefficient, as well as their ratio, showed that the data were thermodynamically consistent. Heat of mixing data were available at 20°C (*5*), and assuming that the temperature did not change them substantially, it could be shown that the value of the integral of $(\Delta H^E/RT)dT$ was negligible, so that the isothermal analysis was valid. Additional calculations were made to verify the influence of dilution on the association constant, by using the information of Posch and Kohler (*10*) and by assuming a linear variation of ln K_2 with concentration between pure and infinite diluted acetic acid. The activity coefficients changed by less than 1%, inspite of the large changes in K_2 as reported above. Inspection of Marek's equations for the activity coefficients showed that the limited influence of K_2 was due to the fact that it appeared as the square root and multiplied by factors that were usually small.

The data indicated in Table III were correlated by means of the Redlich-Kister and the Wilson equation, applying the Simplex method to the calculated values of $G^E = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$.

The following expressions were used for the Wilson equation, as suggested by Nagata and Yamada (*9*):

$$-\frac{G^E}{RT} = x_1 \ln (x_1 + \Lambda_{12}x_2) + x_2 \ln (x_2 + \Lambda_{21}x_1)$$

$$\Lambda_{ij} = (v_j/v_i) \exp\left[-\frac{\lambda_{ij} - \lambda_{ji}}{RT}\right]$$

$$\lambda_{12} - \lambda_{11} = A_1 + A_2\,(T - 273.15)$$

$$\lambda_{21} - \lambda_{22} = B_1 + B_2\,(T - 273.15)$$

The corresponding parameters appear in Table IV, together with the values of the sum of squares of the deviations (*SSQ*).

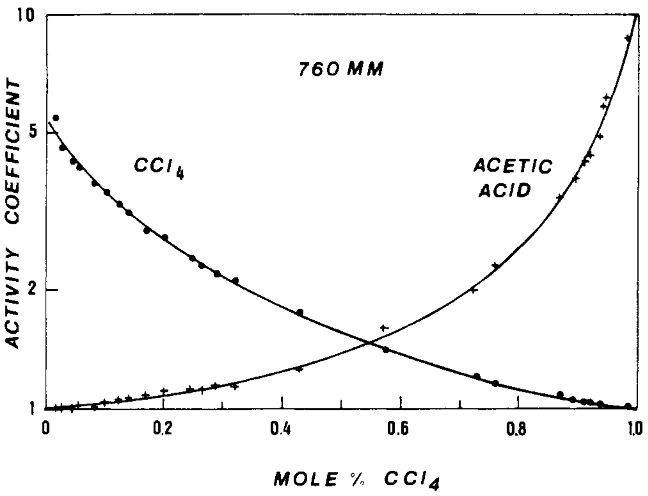

Figure 1. Activity coefficients

Table IV. Parameters of Redlich-Kister and Wilson Equations

		760 mm	417 mm
Redlich-Kister	A	1.53789	1.63322
	B	0.11761	1.28072
	C	0.36467	0.35438
	D	0.22038	−0.15561
	SSQ	0.0957	0.00633
Wilson			
Isothermal	Λ_{12}	0.44353	0.47900
	Λ_{21}	0.19703	0.23875
	SSQ	0.00639	0.00519
Nonisothermal	A_1	50.944	50.873
	A_2	9.0617	11.080
	B_1	45.003	53.733
	B_2	11.872	10.791
	SSQ	0.00470	0.00356

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Nomenclature

G^E = excess Gibbs function
K_2 = dimerization constant for acetic acid, mm^{-1} Hg
n = refractive index
p_i° = vapor pressure of pure component i, mm Hg
R = gas constant
t, T = temperature, °C, K
v_i = molar volume of pure component i, cm^3/mol
x_i = mole fraction of component i

Greek Letters

γ_i = activity coefficient of component i
λ_{ij} = energy of interaction
Λ_{ij} = Wilson parameter

Subscripts

1 = carbon tetrachloride
2 = acetic acid

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Vapor-Liquid Equilibrium of Propionic Acid-Toluene System

John K. Donnelly,[1] **Satyanarayan N. Malpani, and R. Gordon Moore**
Department of Chemical Engineering, The University of Calgary, Calgary, Alta., Canada

Vapor equilibrium data were measured for the system propionic acid–toluene at 500 and 600 mm Hg. These equilibrium data were measured in a vapor recirculating still at temperatures in the range from 95.9° to 127°C, and the analyses were done by refractometry.

Isobaric vapor-liquid equilibrium data were measured for the system propionic acid–toluene. These data were required for the design of a distillation column separating these two components, and no data on this system could be found in the literature. These data were taken at the two pressures of 500 and 600 mm Hg.

Toluene at 99.9% purity (Fisher Scientific Co., Pittsburg) and propionic acid of 99% purity (Anachemia Chemicals Ltd., Montreal) were used with no further purification. The bp of the toluene was 110.6°C, and the bp of the propionic acid was 140.5–141.5°C.

Apparatus and Procedure

The vapor circulating still used was first designed by Othmer (*1*), modified by Othmer (*2–4*), and manufactured by Scientific Glass Apparatus Co., Inc., Bloomfield, N.J. (type JD-3630). The still was equipped with an externally heated thermosiphon which ensured active mix-

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[1] To whom correspondence should be addressed.