

# Association Effects in Propionic Acid Systems

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Vapor-liquid equilibrium data were determined at 760 mm Hg for the systems propionic acid-carbon tetrachloride and propionic acid-methyl isobutyl ketone. Both systems presented strong positive deviations from ideal behavior, and the experimental results were thermodynamically consistent only when the association effects of propionic acid were taken into account. Liquid-phase activity coefficients were correlated with the Redlich-Kister and Wilson equations. Boiling points were predicted by a three-constant empirical correlation.

The purpose of this work is to determine the consequences of association on the vapor-liquid equilibrium of solutions of propionic acid with a simple spherical molecule like carbon tetrachloride and a highly asymmetrical molecule like methyl isobutyl ketone (MIBK). Numerous papers have dealt with the association effects present in carboxylic acid systems (2, 3, 6, 7, 10), the general agreement being that the acid undergoes partial dimerization and even higher polymerizations. For a given acid the degree of association has been dependent on the temperature, the pressure, and the other components present (6, 7, 10). The phenomenon has been analyzed by assuming association in the liquid or vapor phases. It is very difficult to distinguish between deviations of a vapor from ideality and the association of its molecules. McDougall (5) found that even at low pressures the equilibrium constant calculated for the dimerization increased with pressure, a fact that was attributed to the presence of a trimer.

Results obtained by a variety of methods show that the carboxylic acids are associated in hydrocarbons and similar solvents and that in dilute solutions the associated molecule is dimeric. Taylor and Bruton (11) studied the vapor-phase association of formic and propionic acids in the pressure range below 0.1 atm and the temperature range of 50–150°C and found that the hydrogen bond strength in the acids increased in the order formic  $\ll$  acetic  $<$  propionic. Their data for propionic yielded a heat of dissociation much lower than that reported by McDougall (5). Liszi (4) determined the vapor-liquid equilibrium of the system propionic acid-carbon tetrachloride at 30°, 40°, 50°, 60°, and 70°C and found that the acid was almost completely dimerized in the liquid phase. He was thus able to analyze the ternary system monomer-dimer-solvent as a binary one and correlate his results by simple material balances. The activity coefficients were not reported.

## Experimental

**Purity of materials.** Analytical grade reagents purchased from Merck and Fluka were used without further purification after gas chromatography analysis failed to show any significant impurities, particularly water. Physical properties of the pure components appear in Table I.

**Apparatus and procedure.** An all-glass modified Dvorak and Boublik recirculation still (7) was used in the equilibrium determinations. The experimental features have been described previously (13). Analysis of the mixtures of propionic acid-carbon tetrachloride were made at 20°C with a Bausch

& Lomb Abbe-3L precision refractometer which gave direct readings to four significant figures and estimated values reproducible to the nearest 0.00025. The calibration data appear in Table II and can be represented by a straight line so that the accuracy in estimating the concentration data is at least 0.005 concentration units.

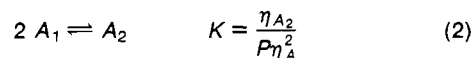
The analysis of propionic acid and methyl isobutyl ketone (MIBK) mixtures was done by gas chromatography on a Packard-Becker Model 417 apparatus provided with an Autolab Model 6300 integrator and a 0.2  $\times$  100-cm column filled with 3% OV-225 on 100/120 Gas Chrom Q. Injector and column temperatures were 220° and 120°C, respectively. Mixtures of known weight composition were analyzed to determine the proper calibration factors. Concentration measurements are believed to be accurate to  $\pm 0.5\%$ .

## Results

Constant pressure equilibrium determinations were made at 760 mm Hg, and the experimental results appear in Tables III and IV. Activity coefficients calculated from the equation

$$\gamma_i = P_{y_i}/P_i^{\circ} x_i \quad (1)$$

were thermodynamically inconsistent because Equation 1 does not include association effects. Results were then correlated with the following equations, based on the models developed by Marek and Standart (6, 7) and Tamir and Wisniak (10). Assuming that A is the only chemical species undergoing association in the vapor phase,



the true mole fraction  $\eta_{A_1}$  of the monomer is

Table I. Physical Constants of Pure Compounds

Index	Compound	Refractive index at 20°C	Bp, °C, 760 mm
1	Propionic acid	1.3860 1.3865 (12)	140.7 140.83 (12)
2	Carbon tetrachloride	1.4600 1.4601 (12)	76.4 76.54 (12)
3	Methyl isobutyl ketone	1.3952 1.3957 (12)	116.3 116.5 (12)

Table II. Refractive Index at 20°C of Mixtures of Propionic Acid(1) and Carbon Tetrachloride(2)

$x_1$	$n$	$x_1$	$n$
0.0000	1.4600	0.7900	1.4025
0.0284	1.4570	0.8090	1.4015
0.0970	1.4520	0.8144	1.4005
0.2357	1.4435	0.8430	1.3985
0.3510	1.4355	0.8553	1.3970
0.3957	1.4317	0.8914	1.3947
0.4175	1.4308	0.9112	1.3930
0.4877	1.4255	0.9232	1.3919
0.6283	1.4155	0.9427	1.3895
0.6708	1.4121	0.9774	1.3875
0.6991	1.4100	1.0000	1.3865
0.7450	1.4060		

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Table III. Experimental Vapor-Liquid Equilibrium Data for System Propionic Acid(1)–Carbon Tetrachloride(2)

$t_{exp}$	$t_{calc}^a$	$x_1$	$y_1$	$\gamma_1$	$\gamma_2$
77.27	76.67	0.045	0.011	4.192247	1.011600
80.15	79.85	0.210	0.032	1.756726	1.104283
83.58	84.29	0.380	0.057	1.291108	1.248965
84.10	84.54	0.390	0.059	1.267804	1.248475
87.03	87.16	0.490	0.076	1.097677	1.354994
87.27	87.43	0.500	0.077	1.077786	1.371591
89.37	88.79	0.545	0.090	1.034347	1.406045
90.08	89.28	0.560	0.094	1.016111	1.420789
91.87	92.02	0.630	0.118	1.000647	1.577936
94.65	94.07	0.670	0.145	1.002792	1.603434
97.90	97.98	0.730	0.185	0.996796	1.735102
99.05	99.58	0.750	0.200	0.993439	1.793284
104.00	104.38	0.800	0.255	0.973183	1.867784
113.20	112.81	0.865	0.398	0.993012	1.864729
115.20	115.14	0.880	0.435	0.995490	1.900112
119.45	120.51	0.911	0.525	1.007323	2.010704
122.40	122.60	0.922	0.560	0.979753	2.002422
129.60	128.89	0.952	0.700	0.970509	1.974271
130.20	129.57	0.955	0.715	0.972137	1.984881
136.95	136.82	0.985	0.890	0.988058	2.116056

<sup>a</sup> From Equation 15.

Table IV. Experimental Vapor-Liquid Equilibria Data Propionic Acid(1)–Methyl Isobutyl Ketone(3)

$t_{exp}$	$t_{calc}^a$	$x_1$	$y_1$	$\gamma_1$	$\gamma_3$
117.00	117.38	0.075	0.027	1.26830	1.03009
118.52	118.38	0.124	0.050	1.23931	1.02097
119.32	119.39	0.168	0.073	1.21898	1.03012
119.37	119.75	0.183	0.082	1.22710	1.03936
121.44	121.20	0.240	0.126	1.23823	1.01435
121.75	121.53	0.253	0.133	1.21467	1.01673
123.06	122.82	0.302	0.170	1.18741	1.01436
124.62	124.61	0.370	0.220	1.13390	1.02613
125.42	125.37	0.399	0.244	1.11524	1.02717
128.00	128.40	0.520	0.343	1.04286	1.07495
130.20	130.29	0.600	0.430	1.02296	1.08624
130.47	130.66	0.616	0.450	1.02626	1.09183
131.20	131.10	0.635	0.480	1.03029	1.07646
133.37	133.14	0.725	0.585	1.00791	1.11963
134.80	134.62	0.788	0.680	1.01874	1.12117
135.44	135.40	0.820	0.713	1.00524	1.18067
135.90	135.75	0.834	0.735	1.00450	1.17874
136.00	135.98	0.843	0.746	1.00457	1.19740
136.40	136.56	0.865	0.772	1.00018	1.25126
138.35	138.68	0.938	0.893	1.00917	1.28496

<sup>a</sup> From Equation 15.

Table V. Antoine Constants

Index	Compound	$\alpha_i$	$\beta_i$	$\delta_i$
1	Propionic acid	7.5476	1617.06	205.67
2	Carbon tetrachloride	6.9339	1242.43	230.10
3	Methyl isobutyl ketone	6.6727	1168.41	191.94

Table VI. Redlich-Kister and Wilson Constants

System	Redlich-Kister							
	$a(i)$	$b(i)$	$c(i)$	$a(j)$	$b(j)$	$c(j)$	$\Lambda_{ij}$	$\Lambda_{ji}$
Propionic acid–CCl <sub>4</sub>	1.1741	–3.8239	3.2687	1.9756	–4.8926	3.267	0.12030	1.215
Propionic acid–MIBK	1.3430	–4.4459	4.7894	4.2539	–8.3272	4.7894	1.1019	0.67094

$$\eta_{A_1} = \frac{n_{A_1}}{n_{A_1} + n_{A_2} + n_B} \quad (3)$$

where  $n_i$  is the number of moles of a given species. The relation between the stoichiometric mole fraction  $y_A$  and the true mole fraction is

$$y_A = \frac{\eta_{A_1} + 2\eta_{A_2}}{1 + \eta_{A_2} + \eta_B} = \frac{\eta_{A_1} + 2KP\eta_{A_1}^2}{1 + 2KP\eta_{A_1}^2 + \eta_B} \quad (4)$$

The vapor pressure of the pure substance,  $P_{A_1}^\circ$ , is the sum of the partial pressures of the monomers  $P_{A_1}^\circ$  and  $P_{A_2}^\circ$ , so that

$$P_A^\circ = P_{A_1}^\circ + P_{A_2}^\circ = P_{A_1}^\circ + KP_{A_1}^{\circ 2} \quad (5)$$

$$P_{A_1}^\circ = \frac{-1 + \sqrt{1 + 4KP_A^\circ}}{2K} \quad (6)$$

Equation 1 can then be modified to take into account association effects as follows

$$Py_A Z_A = \gamma_A X_A P_{A_1}^\circ \quad (7)$$

where

$$Z_A = \frac{\eta_{A_1}}{y_A} \quad (8)$$

Knowledge of the dimerization constant, the vapor pressure of the pure component, and the apparent composition allows calculation of  $\gamma_A$  by the simultaneous solution of Equations 4, 6, and 7. Similar equations can be developed for the nonassociating species. The calculation activity coefficients appear in Tables III and IV. Area tests for the individual activity coefficients, as well as their ratio, showed that the data were thermodynamically consistent.

The physical properties used were as follows: dimerization constant of propionic acid (17)

$$\log K = -10.843 + \frac{3316}{t + 273.15} \quad (9)$$

Vapor pressures were expressed according to the Antoine Equation 12:

$$\log P_i^\circ = \alpha_i - \frac{\beta_i}{t + \delta_i} \quad (10)$$

The constants  $\alpha_i$ ,  $\beta_i$ , and  $\delta_i$  appear in Table V.

The activity coefficients reported in Tables III and IV were correlated by means of the following Redlich-Kister expansion (9):

$$\ln \gamma_i = a(i)x_j^2 + b(i)x_j^3 + c(i)x_j^4 \quad (11)$$

$$\ln \gamma_j = a(j)x_i^2 + b(j)x_i^3 + c(j)x_i^4 \quad (12)$$

with an average relative error of less than 6%. The corresponding coefficients appear in Table VI.

The experimental data were also correlated by the Wilson Equation 8:

$$\ln \gamma_i = -\ln(x_i + \Lambda_{ij}x_j) + x_j \left[ \frac{\Lambda_{ij}}{x_i + \Lambda_{ij}x_j} - \frac{\Lambda_{ji}}{\Lambda_{ji}x_i + x_j} \right] \quad (13)$$

$$\ln \gamma_j = -\ln(x_j + \Lambda_{ji}x_i) - x_i \left[ \frac{\Lambda_{ji}}{x_j + \Lambda_{ji}x_i} - \frac{\Lambda_{ij}}{\Lambda_{ij}x_j + x_i} \right] \quad (14)$$

Table VII. Correlation of Boiling Points

System	$C_0$	$C_1$	$C_2$	Rmsd
Propionic acid- CCl <sub>4</sub>	-82.367	-69.626	-52.858	0.509
Propionic acid- MIBK	-2.0949	-0.23050	-10.144	0.215

Analyses of the activity coefficients for both systems show that the one formed by the spherical solvent CCl<sub>4</sub> presents much larger deviations from ideal behavior than that constituted by a highly asymmetrical molecule like MIBK.

Boiling points of the binary system were correlated with the equation suggested by Wisniak and Tamir (14):

$$T = x_1 T_1^{\circ} + x_2 T_2^{\circ} + \omega + x_1 x_2 \sum_0^k C_k (x_1 - x_2)^k \quad (15)$$

$$\omega = x_1 \ln (y_1/x_1) + x_2 \ln (y_2/x_2) \quad (16)$$

The corresponding constants appear in Table VII together with the root-mean-square deviation.

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#### Nomenclature

$\alpha, \beta, \delta$  = constants, Equation 10

$a(i), b(i), c(i)$  = constants, Equation 11 and 12

$C_k$  = constant, Equation 15

$K$  = dimerization constant, mm<sup>-1</sup> Hg, Equation 1

$n$  = number of experimental points, mol

$P$  = overall pressure, mm Hg

$P_i^{\circ}$  = vapor pressure of species  $i$  pure, mm Hg

rmsd = root-mean-square deviation,  $\sqrt{\sum(t_{\text{exp}} - t_{\text{calc}})^2/n}$

$t, T$  = temperature, °C, K

$T_i^{\circ}$  = boiling temperature of component  $i$  pure at pressure  $P, K$

$x_i, y_i$  = mole fraction composition of component  $i$  in the liquid and vapor phases

$\gamma_i$  = activity coefficient of component  $i$

$\Delta_{ij}, \Lambda_{ji}$  = Wilson constants, Equations 13 and 14

$\eta_i$  = true mole fraction, Equation 3

#### Subscripts

calc = calculated

exp = experimental

$i$  = component  $i$

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