Activity of Water in Solution with Tetrahydrofuran

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The thermodynamic properties, relative volatility, activity coefficient, and activity of the tetrahydrofuran-water system were measured at the normal boiling temperature over the total range of concentration. Special emphasis was placed on measurements in the range from 0 to 14 mol % tetrahydrofuran. An activity minimum of 0.793 was found at a concentration of 2.8 mol % tetrahydrofuran.

The thermodynamic properties of the tetrahydrofuran (THF)-water system were reported by Cigna and Sebastiani (2) and Arm (1), but too few measurements were made in the low THF concentration range to find an anomaly which is reported here.

Several workers (2, 7, 8, 10) noticed in the concentration range from 0 to 15 mol % THF that its gas hydrate freezing curve contains several breaks with concentration. The same behavior was found in the viscosity curve (9), and although THF and water are miscible over the whole concentration range, the solution appears to have a hazy blue color at low THF concentrations (9). Ferguson (5) proposed that the reason an ether such as THF is completely soluble in water is because of association between it and water.

Glew et al. (6) showed that water in dilute aqueous solutions of ethylene oxide, *t*-butyl alcohol, dioxan, and tetrahydrofuran has an abnormally high excess molar volume and that the dilute solutions exhibited positive pmr chemical shifts compared to water. They proposed that the presence of the solute caused the water to build up a hydrogen-bonded shell around it, the effect of which is mainly evident at low solute concentrations. Because of the possibility of an abnormal activity behavior suggested by the physical characteristics of this system at low concentrations, a careful study was made of the activity of the components over the whole concentration range but especially over the range of 0–14 mol % THF where 464 measurements were made.

Experimental

Boiling point-concentration measurements were made at 760 mm Hg with a modified Cottrell-Choppin molecular-weight apparatus. The main modification was in the technique used to nucleate boiling. A fine nichrome heating coil was placed under the pump hood and connected through the glass with platinum wire seals. The voltage to this coil was adjusted by a Variac transformer, adding only enough heat so that if the transformer setting were 1 V lower, boiling would stop. The main heat supply was from a wrapping of asbestos-insulated heating coil on the outside of the apparatus. As a safety note, previous experience with this system with boiling stones which were not changed regularly resulted in a spectacular explosion.

A second modification to the standard equipment was a bubbler-type back-pressure regulator connected to the condenser which allowed the pressure in the apparatus to be adjusted to 760 mm Hg with varying atmospheric pressure.

Temperatures were measured by a platinum-resistance thermometer in one set of measurements (3) and with a $50-100^{\circ}$ C dropping differential Beckman graduated to

0.01°C in the low concentration range. Both instruments were calibrated by use of a Hewlett Packard Model 2801A quartz thermometer in a high-precision bath.

Concentrations were measured with a Bausch and Lomb precision refractometer calibrated with accurately prepared solutions. Fisher-certified grade tetrahydrofuran was used in all measurements.

Data

Table I shows both the raw experimental data and the calculated values of relative volatility, activity coefficient, and activity for both tetrahydrofuran (subscript 1) and water. Each of the points in the low THF concentration range is the average of between four and seven points at the same liquid concentration. The standard deviation from the mean was calculated to be an average value of ± 0.08 for the temperature and ± 0.01 for the vapor composition. From these standard deviations, the standard deviation from the mean for the activity of water (a_2) would be ± 0.006 , and for the activity of THF (a_1), ± 0.035 .

Calculation of the thermodynamic functions was done by use of the usual defining equations for the functions plus values of vapor pressure taken from handbooks.

A check on the thermodynamic consistency of the data over the total concentration range was made with the equation:

$$\int_{0}^{1.0} \log \left(\frac{\gamma_1}{\gamma_2}\right) dx = 0$$

In the plot of log (γ_1/γ_2) vs. x, the difference between the positive and negative areas was only 0.9%. This indicates that the abnormal behavior at low THF concentrations, which should not follow the simple Gibbs-Duhem equation, has not been shown up by the overall test.

Discussion

The main point of interest in this work is the low THF concentration range. To illustrate the type of behavior that has been noted, the activities at the normal boiling points are plotted vs. THF concentration in Figure 1, and the low concentration range is shown in Figure 2 for the water activity only.

Previously reported data on this system (1, 2) agree well with this data above 15 mol % THF. However, too few points were taken in the low concentration range to observe the dip in water activity. Since many other unusual behaviors (6) are exhibited by this system in this concentration range, it is hoped that this new activity data will explain some of them.

The sharp dip in the activity of water with the addition of small amounts of the THF indicates that a more stable environment has been produced. It has been proposed (6) that strong water-water hydrogen bonding causes the water molecules to orient themselves around the solute molecules. If this structured water can be construed as a separate phase in the mixture (possible reason for blue haze), then the apparent thermodynamic inconsistency at the low concentrations can be explained.

Figure 2 does show some hint of the same types of concentration discontinuities in the activity of water as

 Table i. Measured and Calculated Thermodynamic Data for

 Tetrahydrofuran(1)-Water Solutions

fraction THF volatility fraction) ⁻¹ Activity x1 y1 y2 y2 q1 q2 0.02 0.23 93.0 149.1 0.00671 52.8 0.997 0.106 0.995 0.013 0.65 73.70 141.0 0.0079 39.1 0.985 0.588 0.997 0.013 0.67 72.90 12.0 0.00834 28.4 0.887 0.528 0.890 0.020 0.71 72.90 11.5 0.00897 20.7 0.518 0.579 0.793 0.028 0.72 72.90 87.8 0.0114 20.0 0.827 0.588 0.802 0.031 0.73 71.68 76.6 0.0131 17.8 0.860 0.681 0.838 0.802 0.033 0.73 71.68 74.4 0.0131 17.8 0.864 0.618 0.839 0.040 0.74 69.85 6.73 0.0144 16.5 0.822	Mole		Relative		(Mole				
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0.018 0.69 72.90 121.4 0.0023 30.7 0.907 0.552 0.880 0.022 0.71 72.90 110.5 0.00897 26.0 0.837 0.572 0.819 0.028 0.72 72.90 87.8 0.0114 20.0 0.817 0.579 0.793 0.029 0.73 72.50 87.8 0.0112 19.0 0.827 0.588 0.802 0.031 0.73 71.54 74.6 0.0121 18.5 0.832 0.591 0.864 0.033 0.73 71.56 74.4 0.0131 17.8 0.864 0.618 0.833 0.036 0.73 71.56 74.4 0.0141 16.5 0.873 0.822 0.831 0.038 0.73 70.36 66.3 0.0144 16.5 0.833 0.634 0.848 0.840 0.849 0.040 0.74 69.85 67.3 0.0161 15.1 0.984 0.845	0.013	0.65	73.70	141.0	0.00709	39.1	0.985	0.508	0.972
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0.038 0.73 70.36 68.3 0.0146 16.3 0.873 0.624 0.843 0.040 0.74 69.98 66.4 0.0153 15.7 0.894 0.643 0.849 0.041 0.74 69.98 66.4 0.0157 15.5 0.922 0.649 0.864 0.043 0.74 68.62 61.2 0.0161 15.5 0.922 0.668 0.882 0.044 0.74 68.62 61.2 0.0167 14.7 0.934 0.677 0.891 0.045 0.74 68.64 58.7 0.0170 14.4 0.937 0.679 0.893 0.048 0.74 68.04 56.7 0.0170 14.4 0.950 0.690 0.903 0.050 0.75 68.02 55.5 0.0180 13.8 0.951 0.690 0.903 0.051 0.75 67.16 51.7 0.0194 13.0 0.966 0.700 0.913 0.055 </td <td>0.037</td> <td>0.73</td> <td>70.88</td> <td>71.3</td> <td>0.0140</td> <td>16.8</td> <td>0.869</td> <td>0.622</td> <td>0.837</td>	0.037	0.73	70.88	71.3	0.0140	16.8	0.869	0.622	0.837
0.039 0.73 7.36 68.3 0.0149 16.3 0.633 0.646 0.861 0.040 0.74 69.98 65.4 0.0153 15.7 0.894 0.643 0.861 0.042 0.74 69.70 64.2 0.0156 15.5 0.902 0.668 0.882 0.044 0.74 68.92 63.7 0.0161 15.1 0.918 0.664 0.882 0.044 0.74 68.62 61.2 0.0161 15.1 0.931 0.675 0.889 0.045 0.74 68.45 59.9 0.0170 14.4 0.937 0.679 0.893 0.044 0.75 68.04 56.7 0.0176 14.1 0.960 0.904 0.951 0.750 0.893 0.045 0.75 67.70 54.8 0.0182 13.7 0.960 0.993 0.964 0.955 0.700 0.913 0.055 0.75 67.14 51.3 0.0194 13.	0.038	0.73	/0./5	69.6 69.5	0.0144	16.5	0.8/3	0.625	0.840
0.041 0.74 69.96 65.44 0.0153 15.7 0.893 0.643 0.858 0.042 0.74 69.97 64.2 0.0155 15.5 0.902 0.643 0.858 0.043 0.74 68.92 63.7 0.0157 15.5 0.922 0.668 0.882 0.044 0.74 68.26 61.2 0.0161 15.1 0.918 0.664 0.878 0.045 0.74 68.26 51.2 0.0170 14.4 0.937 0.679 0.889 0.044 0.74 68.21 57.7 0.0176 14.1 0.950 0.690 0.903 0.050 0.75 68.02 55.5 0.0180 13.8 0.951 0.669 0.903 0.051 0.75 67.02 53.8 0.0182 13.3 0.967 0.703 0.913 0.052 0.75 67.14 51.3 0.0192 12.8 0.982 0.713 0.926 0.055<	0.039	0.75	70.30 60.85	67 3	0.0140	16.5	0.005	0.034	0.849
0.042 0.74 69.70 64.22 0.0156 15.5 0.902 0.649 0.864 0.043 0.74 68.92 63.7 0.0157 15.5 0.922 0.668 0.882 0.044 0.74 68.91 62.0 0.0161 15.1 0.918 0.664 0.878 0.045 0.74 68.62 61.2 0.0167 14.7 0.934 0.677 0.891 0.047 0.74 68.21 57.7 0.0170 14.4 0.937 0.690 0.904 0.050 0.75 68.04 56.7 0.0176 14.1 0.950 0.690 0.904 0.051 0.75 67.70 54.8 0.0182 13.7 0.960 0.698 0.911 0.052 0.75 67.14 51.3 0.0194 13.0 0.966 0.700 0.913 0.055 0.75 67.14 51.3 0.0205 12.4 0.982 0.714 0.927 0.55 </td <td>0.040</td> <td>0.74</td> <td>69.05</td> <td>65.4</td> <td>0.0143</td> <td>15.7</td> <td>0.894</td> <td>0.643</td> <td>0.858</td>	0.040	0.74	69.05	65.4	0.0143	15.7	0.894	0.643	0.858
0.043 0.74 68.92 63.7 0.0157 15.5 0.922 0.668 0.882 0.044 0.74 68.92 63.7 0.0161 15.1 0.918 0.664 0.78 0.045 0.74 68.54 59.9 0.0167 14.7 0.934 0.675 0.889 0.047 0.74 68.46 58.7 0.0170 14.4 0.937 0.679 0.893 0.048 0.74 68.21 57.7 0.0173 14.3 0.944 0.655 0.899 0.049 0.75 68.04 56.7 0.0182 13.7 0.960 0.990 0.050 0.75 67.62 53.8 0.0181 13.5 0.960 0.913 0.051 0.75 67.14 51.3 0.0191 13.0 0.965 0.712 0.922 0.056 0.75 67.14 51.3 0.0208 12.3 0.993 0.723 0.913 0.057 0.75 66.55 <td>0.042</td> <td>0.74</td> <td>69.70</td> <td>64.2</td> <td>0.0156</td> <td>15.5</td> <td>0.902</td> <td>0.649</td> <td>0.864</td>	0.042	0.74	69.70	64.2	0.0156	15.5	0.902	0.649	0.864
0.044 0.74 69.10 62.0 0.0161 15.1 0.918 0.664 0.878 0.045 0.74 68.52 61.2 0.0163 15.0 0.931 0.675 0.889 0.047 0.74 68.54 59.9 0.0170 14.4 0.937 0.679 0.833 0.048 0.74 68.21 57.7 0.0173 14.3 0.944 0.680 0.899 0.049 0.75 68.02 55.5 0.0180 13.8 0.951 0.690 0.903 0.051 0.75 67.62 53.8 0.0182 13.7 0.960 0.690 0.913 0.052 0.75 67.62 53.8 0.0189 13.3 0.967 0.700 0.913 0.055 0.75 67.14 51.3 0.0199 12.8 0.982 0.714 0.927 0.056 0.75 67.10 49.4 0.0202 12.3 0.940 0.931 0.652 0.75 66.5	0.043	0.74	68.92	63.7	0.0157	15.5	0.922	0.668	0.882
0.045 0.74 68.62 61.2 0.0163 15.0 0.931 0.675 0.889 0.046 0.74 68.46 58.7 0.0170 14.4 0.937 0.679 0.893 0.048 0.74 68.21 57.7 0.0173 14.3 0.944 0.685 0.899 0.049 0.75 68.02 55.5 0.0180 13.8 0.951 0.690 0.904 0.050 0.75 67.02 53.8 0.0182 13.7 0.960 0.698 0.911 0.052 0.75 67.64 51.7 0.0194 13.0 0.967 0.700 0.913 0.055 0.75 67.14 51.3 0.0195 13.0 0.967 0.700 0.913 0.055 0.75 67.14 51.3 0.0191 13.8 0.967 0.713 0.926 0.056 0.75 67.08 50.4 0.0191 12.8 0.982 0.714 0.927 0.057 </td <td>0.044</td> <td>0.74</td> <td>69.10</td> <td>62.0</td> <td>0.0161</td> <td>15.1</td> <td>0.918</td> <td>0.664</td> <td>0.878</td>	0.044	0.74	69.10	62.0	0.0161	15.1	0.918	0.664	0.878
0.046 0.74 68.45 59.9 0.0167 14.7 0.934 0.677 0.891 0.047 0.74 68.21 57.7 0.0173 14.3 0.944 0.685 0.899 0.048 0.74 68.21 57.7 0.0176 14.1 0.950 0.690 0.903 0.050 0.75 68.02 55.5 0.0180 13.8 0.951 0.690 0.904 0.051 0.75 67.62 53.8 0.0182 13.7 0.960 0.698 0.911 0.052 0.75 67.64 51.7 0.0194 13.0 0.965 0.700 0.913 0.055 0.75 67.14 51.3 0.0199 12.8 0.982 0.714 0.922 0.056 0.75 67.08 50.4 0.0208 12.3 0.993 0.228 0.933 0.057 0.75 66.93 48.7 0.0228 13.0 0.728 0.940 0.056 0.75 <td>0.045</td> <td>0.74</td> <td>68.62</td> <td>61.2</td> <td>0.0163</td> <td>15.0</td> <td>0.931</td> <td>0.675</td> <td>0.889</td>	0.045	0.74	68.62	61.2	0.0163	15.0	0.931	0.675	0.889
0.047 0.74 68.46 58.7 0.0170 14.4 0.937 0.679 0.893 0.048 0.74 68.01 57.7 0.0173 14.3 0.944 0.685 0.899 0.049 0.75 68.04 56.7 0.0176 14.1 0.950 0.690 0.903 0.050 0.75 67.70 54.8 0.0182 13.7 0.960 0.690 0.913 0.052 0.75 67.62 53.8 0.0186 13.5 0.965 0.700 0.913 0.055 0.75 67.14 51.3 0.0199 12.8 0.982 0.714 0.927 0.056 0.75 67.10 49.4 0.0202 12.5 0.982 0.714 0.927 0.057 0.75 67.10 49.4 0.0202 12.5 0.982 0.714 0.933 0.056 0.75 66.53 48.7 0.0203 12.4 0.984 0.940 0.962 0.060 </td <td>0.046</td> <td>0.74</td> <td>68.54</td> <td>59.9</td> <td>0.0167</td> <td>14.7</td> <td>0.934</td> <td>0.677</td> <td>0.891</td>	0.046	0.74	68.54	59.9	0.0167	14.7	0.934	0.677	0.891
0.048 0.74 68.21 57.7 0.0173 14.3 0.944 0.685 0.899 0.049 0.75 68.04 56.7 0.0176 14.1 0.950 0.690 0.903 0.050 0.75 67.70 54.8 0.0182 13.7 0.960 0.698 0.911 0.052 0.75 67.62 53.8 0.0189 13.3 0.967 0.700 0.913 0.053 0.75 67.14 51.7 0.0194 13.0 0.965 0.700 0.913 0.055 0.75 67.14 51.3 0.0195 13.0 0.980 0.712 0.925 0.056 0.75 67.10 49.4 0.0202 12.5 0.982 0.714 0.926 0.057 0.75 66.71 48.0 0.0208 12.3 0.993 0.723 0.930 0.056 0.75 66.53 45.8 0.0213 12.0 0.940 0.728 0.940 0.062 </td <td>0.047</td> <td>0.74</td> <td>68.46</td> <td>58.7</td> <td>0.0170</td> <td>14.4</td> <td>0.937</td> <td>0.679</td> <td>0.893</td>	0.047	0.74	68.46	58.7	0.0170	14.4	0.937	0.679	0.893
0.149 0.75 68.04 55.7 0.0176 14.1 0.950 0.790 0.993 0.050 0.75 68.02 55.5 0.0180 13.8 0.951 0.690 0.994 0.051 0.75 67.70 54.8 0.0182 13.7 0.960 0.698 0.911 0.052 0.75 67.62 53.8 0.0189 13.3 0.967 0.703 0.916 0.054 0.75 67.64 51.7 0.0194 13.0 0.965 0.700 0.913 0.055 0.75 67.14 51.3 0.0199 12.8 0.982 0.712 0.925 0.056 0.75 67.08 50.4 0.0208 12.3 0.993 0.723 0.935 0.055 0.75 66.75 48.0 0.0208 12.3 0.993 0.723 0.935 0.060 0.75 66.75 48.0 0.0213 12.0 0.991 0.719 0.931 0.061 0.75 66.40 45.1 0.0221 11.6 1.01 0.732	0.048	0.74	68.21	57.7	0.0173	14.3	0.944	0.685	0.899
0.050 0.75 67.70 54.8 0.0182 13.7 0.960 0.698 0.911 0.051 0.75 67.62 53.8 0.0182 13.7 0.960 0.698 0.911 0.052 0.75 67.61 52.9 0.0189 13.3 0.967 0.700 0.913 0.054 0.75 67.64 51.7 0.0194 13.0 0.965 0.700 0.913 0.055 0.75 67.14 51.3 0.0199 12.8 0.982 0.714 0.927 0.057 0.75 67.10 49.4 0.0208 12.4 0.982 0.718 0.935 0.058 0.75 66.75 48.0 0.0208 12.4 0.984 0.718 0.935 0.060 0.75 66.55 46.6 0.0213 12.0 0.991 0.719 0.931 0.061 0.75 66.34 43.7 0.0228 11.3 1.01 0.732 0.940 0.662 0.75 66.14 43.2 0.0213 11.2 1.02 0.739 <	0.049	0.75	68.04	55./	0.01/6	14.1	0.950	0.690	0.903
0.1052 0.775 67.162 54.78 0.1052 13.7 0.1053 0.1070 0.913 0.053 0.775 67.64 51.7 0.0189 13.3 0.967 0.700 0.913 0.055 0.75 67.14 51.3 0.0195 13.0 0.965 0.712 0.925 0.056 0.75 67.14 51.3 0.0199 12.8 0.980 0.712 0.925 0.056 0.75 67.10 49.4 0.0202 12.5 0.982 0.713 0.926 0.058 0.75 66.93 48.7 0.0202 12.4 0.988 0.718 0.930 0.059 0.75 66.55 46.6 0.0215 11.9 1.00 0.723 0.931 0.061 0.75 66.53 45.8 0.0213 11.2 1.02 0.739 0.940 0.062 0.75 66.34 43.7 0.0228 11.3 1.01 0.732 0.944 0.0	0.050	0.75	67 70	50.5 54 8	0.0180	13.0	0.951	0.090	0.904
0.0530.7567.5152.90.012813.30.9670.7030.9160.0540.7567.6451.70.019413.00.9650.7000.9130.0550.7567.1451.30.019513.00.9800.7120.9250.0560.7567.1049.40.020212.50.9820.7130.9260.0580.7566.9348.70.020512.40.9880.7120.9260.0580.7566.9348.70.020512.40.9880.7130.9300.0590.7566.5546.60.021511.91.000.7230.9350.0600.7566.5546.60.021511.91.000.7280.9400.0620.7566.5345.80.021811.71.000.7280.9400.0630.7566.1443.70.022111.61.010.7320.9440.0650.7566.1443.20.023111.21.020.7360.9470.0680.7566.2642.40.026111.01.020.7370.9480.0690.7566.0741.80.024910.81.020.7420.9530.0700.7565.7640.30.024210.71.020.7410.9520.0700.7565.7640.30.024210.71.020.7410.9570.7665.7639.10.0	0.052	0.75	67.62	53.8	0.0186	13.5	0.963	0.700	0.913
0.054 0.75 67.64 51.7 0.0194 13.0 0.965 0.700 0.913 0.055 0.75 67.14 51.3 0.0195 13.0 0.980 0.712 0.925 0.056 0.75 67.08 50.4 0.0199 12.8 0.982 0.714 0.927 0.057 0.75 67.10 49.4 0.0202 12.5 0.982 0.713 0.926 0.058 0.75 66.93 48.7 0.0208 12.3 0.993 0.723 0.935 0.060 0.75 66.54 46.6 0.0213 12.0 0.991 0.719 0.931 0.061 0.75 66.55 46.6 0.0211 11.6 1.01 0.728 0.940 0.062 0.75 66.44 43.7 0.0228 11.3 1.01 0.734 0.944 0.065 0.75 66.23 41.8 0.0239 10.8 1.02 0.737 0.944 0.066	0.053	0.75	67.51	52.9	0.0189	13.3	0.967	0.703	0.916
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.054	0.75	67.64	51.7	0.0194	13.0	0,965	0.700	0.913
0.056 0.75 67.08 50.4 0.0199 12.8 0.982 0.714 0.927 0.057 0.75 67.10 49.4 0.0202 12.5 0.982 0.713 0.926 0.058 0.75 66.93 48.7 0.0205 12.4 0.988 0.718 0.935 0.060 0.75 66.75 48.0 0.0208 12.3 0.993 0.723 0.935 0.061 0.75 66.55 46.6 0.0213 12.0 0.991 0.719 0.931 0.062 0.75 66.53 45.8 0.0218 11.7 1.00 0.728 0.940 0.063 0.75 66.40 45.1 0.0228 11.3 1.01 0.734 0.944 0.066 0.75 66.24 42.4 0.0231 11.2 1.02 0.736 0.947 0.068 0.75 66.07 41.3 0.0242 10.7 1.02 0.741 0.952 0.070	0.055	0.75	67.14	51.3	0.0195	13.0	0.980	0.712	0.925
0.057 0.75 67.10 49.4 0.0202 12.5 0.982 0.713 0.926 0.058 0.75 66.93 48.7 0.0205 12.4 0.988 0.718 0.930 0.059 0.75 66.75 48.0 0.0208 12.3 0.993 0.723 0.935 0.060 0.75 66.50 47.0 0.0213 12.0 0.991 0.719 0.931 0.061 0.75 66.55 46.6 0.0215 11.9 1.00 0.728 0.940 0.062 0.75 66.34 45.1 0.0221 11.6 1.01 0.732 0.944 0.066 0.75 66.14 43.2 0.0231 11.2 1.02 0.739 0.950 0.067 0.75 66.23 41.8 0.0239 10.8 1.02 0.737 0.948 0.069 0.75 66.07 41.3 0.0242 10.7 1.02 0.741 0.952 0.070 0.75 65.76 39.1 0.0252 10.4 1.03 0.748 0	0.056	0.75	67.08	50.4	0.0199	12.8	0.982	0.714	0.927
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.057	0.75	67.10	49.4	0.0202	12.5	0.982	0.713	0.926
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.058	0.75	66.93	48.7	0.0205	12.4	0.988	0.718	0.930
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.059	0.75	66 90	48.0	0.0208	12.3	0,995	0.723	0.935
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.000	0.75	66 55	47.0	0.0215	11.9	1.00	0.728	0.940
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.062	0.75	66.53	45.8	0.0218	11.7	1.00	0.728	0.940
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.063	0.75	66.40	45.1	0.0221	11.6	1.01	0.732	0.944
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.065	0.75	66.34	43.7	0.0228	11.3	1.01	0.734	0.945
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.066	0.75	66.14	43.2	0.0231	11.2	1.02	0.739	0.950
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.067	0.75	66.26	42.4	0.0236	11.0	1.02	0.736	0.947
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.068	0.75	66.23	41.8	0.0239	10.8	1.02	0./3/	0.948
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.069	0.75	66.02	41.3	0.0242	10.7	1.02	0.741	0.902
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.070	0.75	65 76	40.3	0.0248	10.6	1.02	0.749	0.955
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.072	0.76	65,80	39.7	0.0252	10.4	1.03	0.748	0.959
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.073	0.76	65.76	39.1	0.0256	10.3	1.04	0.749	0,960
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.074	0.76	65.86	38.5	0.0260	10.1	1.03	0.747	0.957
0.077 0.76 65.58 37.1 0.0270 9.80 1.05 0.754 0.965 0.078 0.76 65.66 36.5 0.0274 9.64 1.04 0.752 0.963 0.079 0.76 65.47 36.2 0.0277 9.59 1.05 0.757 0.967 0.080 0.76 65.42 35.7 0.0280 9.48 1.05 0.760 0.969 0.081 0.76 65.44 34.8 0.0284 9.36 1.05 0.758 0.968 0.082 0.76 65.44 34.8 0.0288 9.25 1.05 0.758 0.968 0.083 0.76 65.32 33.9 0.0295 9.07 1.06 0.760 0.970 0.084 0.76 65.25 32.7 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.973 0.088	0.075	0.76	65.87	37.9	0.0264	9.95	1.03	0.746	0.957
0.078 0.76 65.66 36.5 0.0274 9.64 1.04 0.752 0.963 0.079 0.76 65.47 36.2 0.0277 9.59 1.05 0.757 0.967 0.080 0.76 65.42 35.7 0.0280 9.48 1.05 0.760 0.969 0.081 0.76 65.44 35.2 0.0284 9.36 1.05 0.758 0.968 0.082 0.76 65.44 34.8 0.0288 9.25 1.05 0.758 0.968 0.083 0.76 65.38 34.3 0.0291 9.15 1.06 0.760 0.970 0.084 0.76 65.32 33.9 0.0295 9.07 1.06 0.764 0.973 0.086 0.76 65.24 33.1 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.973 0.088	0.077	0.76	65.58	37.1	0.0270	9.80	1.05	0.754	0.965
0.079 0.76 65.47 36.2 0.0277 9.59 1.05 0.757 0.967 0.080 0.76 65.42 35.7 0.0280 9.48 1.05 0.760 0.969 0.081 0.76 65.42 35.7 0.0280 9.48 1.05 0.760 0.969 0.082 0.76 65.44 34.8 0.0284 9.36 1.05 0.758 0.968 0.083 0.76 65.38 34.3 0.0291 9.15 1.06 0.760 0.970 0.084 0.76 65.22 33.9 0.0295 9.07 1.06 0.762 0.971 0.086 0.76 65.24 33.1 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.25 32.7 0.0306 8.78 1.07 0.766 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.977 0.090	0.078	0.76	65.66	36.5	0.0274	9.64	1.04	0.752	0.963
0.080 0.76 65.42 33.7 0.0280 3.48 1.03 0.768 0.968 0.081 0.76 65.45 35.2 0.0284 9.36 1.05 0.758 0.968 0.082 0.76 65.44 34.8 0.0284 9.36 1.05 0.758 0.968 0.083 0.76 65.38 34.3 0.0291 9.15 1.06 0.760 0.970 0.084 0.76 65.22 33.9 0.0295 9.07 1.06 0.762 0.971 0.086 0.76 65.24 33.1 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.25 32.7 0.0306 8.78 1.07 0.763 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.976 0.090 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.977 0.090	0.079	0.76	65.4/	30.Z	0.0277	9.59	1.05	0./5/	0.967
0.082 0.76 65.44 34.8 0.0288 9.25 1.05 0.758 0.968 0.082 0.76 65.38 34.3 0.0291 9.15 1.06 0.760 0.970 0.084 0.76 65.32 33.9 0.0295 9.07 1.06 0.762 0.971 0.086 0.76 65.24 33.1 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.25 32.7 0.0306 8.78 1.07 0.763 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.973 0.090 0.76 65.11 31.6 0.0316 8.53 1.07 0.767 0.977 0.091 0.76 65.07 31.3 0.0320 8.45 1.08 0.769 0.978 0.092	0.080	0.70	65.42	35.7	0.0280	9.40 9.26	1.05	0.758	0,968
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	0.082	0.76	65.44	34.8	0.0288	9.25	1.05	0.758	0.968
0.084 0.76 65.32 33.9 0.0295 9.07 1.06 0.762 0.971 0.086 0.76 65.24 33.1 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.25 32.7 0.0306 8.78 1.07 0.763 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.976 0.090 0.76 65.11 31.6 0.0316 8.53 1.07 0.767 0.977 0.091 0.76 65.07 31.3 0.0320 8.45 1.08 0.769 0.978 0.092 0.76 65.09 30.9 0.0324 8.35 1.08 0.768 0.977	0.083	0.76	65.38	34.3	0.0291	9.15	1.06	0.760	0.970
0.086 0.76 65.24 33.1 0.0302 8.88 1.06 0.764 0.973 0.087 0.76 65.25 32.7 0.0306 8.78 1.07 0.763 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.976 0.090 0.76 65.11 31.6 0.0316 8.53 1.07 0.767 0.977 0.091 0.76 65.07 31.3 0.0320 8.45 1.08 0.769 0.978 0.092 0.76 65.09 30.9 0.0324 8.35 1.08 0.768 0.977	0.084	0.76	65.32	33.9	0.0295	9.07	1.06	0.762	0.971
0.087 0.76 65.25 32.7 0.0306 8.78 1.07 0.763 0.973 0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.976 0.090 0.76 65.11 31.6 0.0316 8.53 1.07 0.767 0.977 0.091 0.76 65.07 31.3 0.0320 8.45 1.08 0.769 0.978 0.092 0.76 65.09 30.9 0.0324 8.35 1.08 0.768 0.977	0.086	0.76	65.24	33.1	0.0302	8.88	1.06	0.764	0.973
0.088 0.76 65.15 32.4 0.0309 8.71 1.07 0.766 0.976 0.090 0.76 65.11 31.6 0.0316 8.53 1.07 0.767 0.977 0.091 0.76 65.07 31.3 0.0320 8.45 1.08 0.769 0.978 0.092 0.76 65.09 30.9 0.0324 8.35 1.08 0.768 0.977	0.087	0.76	65.25	32.7	0.0306	8.78	1.07	0.763	0.973
0.090 0.76 65.07 31.3 0.0310 8.53 1.07 0.767 0.977 0.091 0.76 65.07 31.3 0.0320 8.45 1.08 0.769 0.978 0.092 0.76 65.09 30.9 0.0324 8.35 1.08 0.768 0.977	0.088	0.76	65.15	32.4	0.0309	8.71	1.07	0.766	0.976
0.092 0.76 65.09 30.9 0.0324 8.35 1.08 0.768 0.978	U.U90 0.001	U./6 0.76	00.11 65 07	31.0 21 2	0.0320	8.55 8 / F	1.U/ 1 NR	U./0/ 0 760	U.9// N 979
	0.092	0.76	65.09	30.9	0.0324	8.35	1.08	0.768	0.977

Mc fractio	ole n THF		Relative volatility		(Mole fraction) ⁻¹		Activity	
x 1	y 1	+, ℃	α12	α ₂₁	γ1	γ ₂	a 1	a 2
0.095	0.76	65.09	29.8	0.0336	8.08	1.08	0.768	0.977
0.097	0.76	65.05	29.2	0.0343	7.93	1.08•	0.769	0.978
0.099	0.76	64.92	28.6	0.0350	7.81	1.09	0.773	0.982
0.101	0.76	64.92	28.0	0.0357	7.65	1.09	7.773	0.982
0.102	0.76	64.91	27.7	0.0361	7.60	1.09	0.773	0.982
0.103	0.76	64.89	27.4	0.0365	7.51	1.10	0.774	0.983
0.106	0.76	64.78	26.6	0.0376	7.33	1.10.	0.777	0,985
0.107	0.76	64.74	26.3	0.0380	7.27	1.10	0.778	0.986
0.110	0.76	64.80	25.5	0.0392	7.06	1.11	0.776	0.985
0.113	0.76	64.80	24.7	0.0404	6.87	1.11	0.776	0.985
0.116	0.76	64.72	24.1	0.0416	6.71	1.12	0.779	0.987
0.121	0.76	64.68	23.0	0.0435	6.44	1.12	0.780	0,988
0.125	0.76	64.71	22.1	0.0452	6.23	1.13	0.779	0.987
0.126	0.76	64.72	21.9	0.0457	6.18	1.13	0.779	0.987
0.136	0.76	64.74	20.1	0.0499	5.72	1.14	0.778	0,986
0.150	0.77	64.75	18.5	0.0542	5.30	1.16	0.796	0,987
0.200	0.77	64.25	13.0	0.0768	3.98	1.23	0.796	0.987
0.250	0.77	64.25	9.77	0.102	3.18	1.32	0,796	0,987
0.300	0.77	64.24	7.60	0.132	2.65	1.41	0.796	0.987
0.350	0.77	64.25	6.05	0.165	2.27	1.52	0.796	0.987
0.400	0.77	64.20	4.88	0.205	1.99	1.65	0.797	0.987
0.450	0.77	64.15	3.98	0.251	1.77	1.80	0.798	0,987
0.500	0.77	64.10	3.26	0.307	1.60	1.98	0.799	0,992
0.550	0.77	64.00	2.66	0.375	1.46	2.21	0.802	0.996
0.600	0.77	63.90	2.17	0.461	1.34	2.50	0.805	1.00
0.650	0.77	63.80	1.75	0.570	1.24	2.87	0.807	1.01
0.700	0.77	63.70	1.43	0.697	1.16	3.29	0.815	0.988
0.750	0.78	63.50	1.20	0.831	1.11	3.76	0.834	0.941
0.800	0.80	63.41	1.03	0.975	1.07	4.27	0.859	0.854
0.850	0.83	63.32	0.874	1.14	1.05	4.90	0.892	0.735
0.900	0.87	63.80	0.744	1.34	1.02	5.56	0.918	0.556
0.950	0.92	64.51	0.622	1.61	1.06	6.47	0.952	0.323



Figure 1. Activity of water and tetrahydrofuran as function of THF concentration



Figure 2. Expanded graph of activity of water at low THF concentrations

occurred in the melting point of the hydrate (4, 10), the viscosity (9), and the freezing rate (8) of the solutions. However, the accuracy of the data is not sufficient to make any definitive statement about this phenomena.

Nomenclature

- $a_1 = \text{activity of THF}$
- $a_2 = \text{activity of water}$
- $t = \text{temperature}, ^{\circ}\text{C}$
- $x_1 =$ liquid concentration, mole fraction THF
- $y_1 =$ vapor concentration, mole fraction THF
- α_{12} = relative volatility THF/H₂O
- α_{21} = relative volatility H₂O/THF
- γ_1 = activity coefficient THF (mole fraction THF)⁻¹
- γ_2 = activity coefficient water (mole fraction water)⁻¹

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Molecular Associations in Nonagueous Solvents Thermodynamics of Dye-Dye Interactions in CCl₄ and C₆H₆

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The thermodynamic parameters of the dimerization of 4, 4',4'',4'''-tetraoctadecylsulfonamido copper(11) phthalocyanine in benzene and carbon tetrachloride were determined by an adiabatic calorimetric technique. The values for the dimerization in benzene were $\Delta H_1^\circ = -10$ \pm 1 kcal/mol, $\Delta G_1^{\circ} = -5.6 \pm 0.1$ kcal/mol, and ΔS_1° $= -15 \pm 4$ cal/deg. On the basis of the reported values for the dimerization in benzene, the values for the dimerization in carbon tetrachloride were estimated to be $\Delta H_1^{\circ} \approx -13$ kcal/mol, $\Delta G_1^{\circ} \approx -8.7$ kcal/mol, and $\Delta S_1{}^{o} \approx \, -15 \; \text{cal/deg.}$ These results are compared with previously reported values for the dimerization of aqueous metal phthalocyanine ions and other dimerizations in solvents of low dielectric strength.

Metal phthalocyanine dyes, of which 4, 4', 4'', 4'''tetraoctadecyisulfonamido copper(II) phthalocyanine, CuPc (Figure 1), is an example, provide analogs to the biologically important porphyrin skeleton of chlorophyll

and the heme moiety of hemoglobin. Additionally, the solid-state interactions of these dyes can be simulated in solution by matching solvent properties and structure solubility characteristics (6). Several spectroscopic studies of water-soluble metal complexes of tetrasulfonated phthalocyanine ions (1, 4) and descriptions of the dimerization process (7, 9) of these charged species have appeared in the literature. However, until recently, little work had been done on phthalocyanine metal(11) dyes in solvents of low dielectric strength (6), where the impetus toward dimerization is the dye-dye interaction. Therefore, it is our purpose to investigate systematically the parameters of dimerization in solvents of low dielectric constant, specifically benzene and carbon tetrachloride.

Experimental

Calorimetric titration measurements of enthalpies of dilution of CuPc in benzene and carbon tetrachloride were made with the Tronac 450 adiabatic calorimeter coupled with the Tronac 1040 temperature controller. The titration apparatus was modified to include a Metrohm Herisau Dosimat automatic piston buret, coupled to a precision synchronous motor for delivery of solutions to

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