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°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

Mole fraction THF			Relative volatility		(Mole fraction)$^{-1}$		Activity	
x_1	y_1	t, °C	α_{12}	α_{21}	γ_1	γ_2	a_1	a_2
0.002	0.23	93.0	149.1	0.00671	52.8	0.997	0.106	0.995
0.005	0.42	85.70	144.1	0.00694	46.8	0.995	0.234	0.990
0.013	0.65	73.70	141.0	0.00709	39.1	0.985	0.508	0.972
0.018	0.69	72.90	121.4	0.00823	30.7	0.907	0.552	0.890
0.020	0.71	72.90	120.0	0.00834	28.4	0.850	0.568	0.833
0.022	0.72	72.90	111.5	0.00897	26.0	0.837	0.572	0.819
0.028	0.72	72.92	91.0	0.0109	20.7	0.816	0.579	0.793
0.029	0.72	72.90	87.8	0.0114	20.0	0.817	0.579	0.793
0.031	0.73	72.50	82.7	0.0121	19.0	0.827	0.588	0.802
0.032	0.73	72.32	80.3	0.0125	18.5	0.832	0.591	0.806
0.033	0.73	71.84	78.6	0.0127	18.2	0.844	0.601	0.816
0.034	0.73	71.62	76.6	0.0131	17.8	0.850	0.606	0.821
0.035	0.73	71.58	74.4	0.0134	17.3	0.851	0.607	0.822
0.036	0.73	71.06	73.1	0.0137	17.2	0.864	0.618	0.833
0.037	0.73	70.88	71.3	0.0140	16.8	0.869	0.622	0.837
0.038	0.73	70.75	69.6	0.0144	16.5	0.873	0.625	0.840
0.039	0.73	70.36	68.3	0.0146	16.3	0.883	0.634	0.849
0.040	0.74	69.85	67.3	0.0149	16.1	0.896	0.646	0.861
0.041	0.74	69.98	65.4	0.0153	15.7	0.894	0.643	0.858
0.042	0.74	69.70	64.2	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	69.10	62.0	0.0161	15.1	0.918	0.664	0.878
0.045	0.74	68.62	61.2	0.0163	15.0	0.931	0.675	0.889
0.046	0.74	68.54	59.9	0.0167	14.7	0.934	0.677	0.891
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	0.685	0.899
0.049	0.75	68.04	56.7	0.0176	14.1	0.950	0.690	0.903
0.050	0.75	68.02	55.5	0.0180	13.8	0.951	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	67.62	53.8	0.0186	13.5	0.963	0.700	0.913
0.053	0.75	67.51	52.9	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	0.0195	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	0.0205	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	66.90	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	66.53	45.8	0.0218	11.7	1.00	0.728	0.940
0.063	0.75	66.40	45.1	0.0221	11.6	1.01	0.732	0.944
0.065	0.75	66.34	43.7	0.0228	11.3	1.01	0.734	0.945
0.066	0.75	66.14	43.2	0.0231	11.2	1.02	0.739	0.950
0.067	0.75	66.26	42.4	0.0236	11.0	1.02	0.736	0.947
0.068	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	66.03	40.7	0.0246	10.6	1.02	0.742	0.953
0.071	0.75	65.76	40.3	0.0248	10.6	1.03	0.749	0.960
0.072	0.76	65.80	39.7	0.0252	10.4	1.03	0.748	0.959
0.073	0.76	65.76	39.1	0.0256	10.3	1.04	0.749	0.960
0.074	0.76	65.86	38.5	0.0260	10.1	1.03	0.747	0.957
0.075	0.76	65.87	37.9	0.0264	9.95	1.03	0.746	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	65.45	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	0.762	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
0.095	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

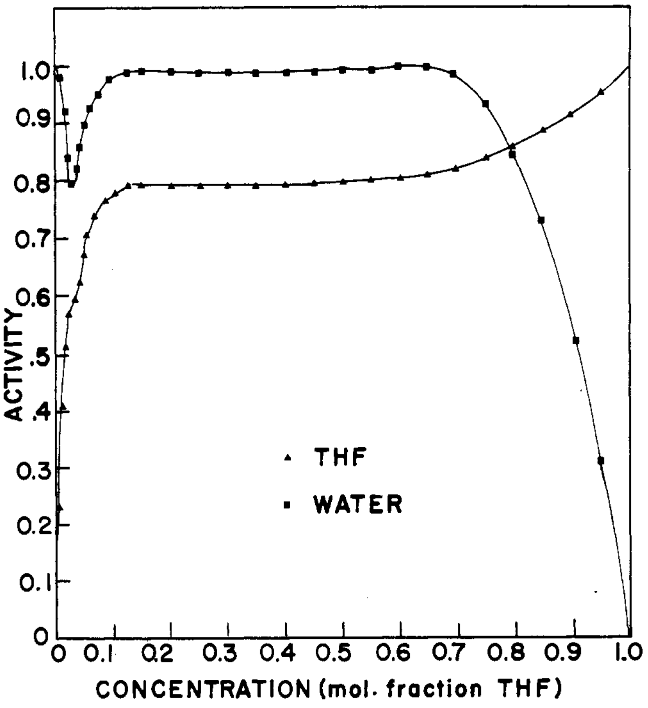

Figure 1. Activity of water and tetrahydrofuran as function of THF concentration

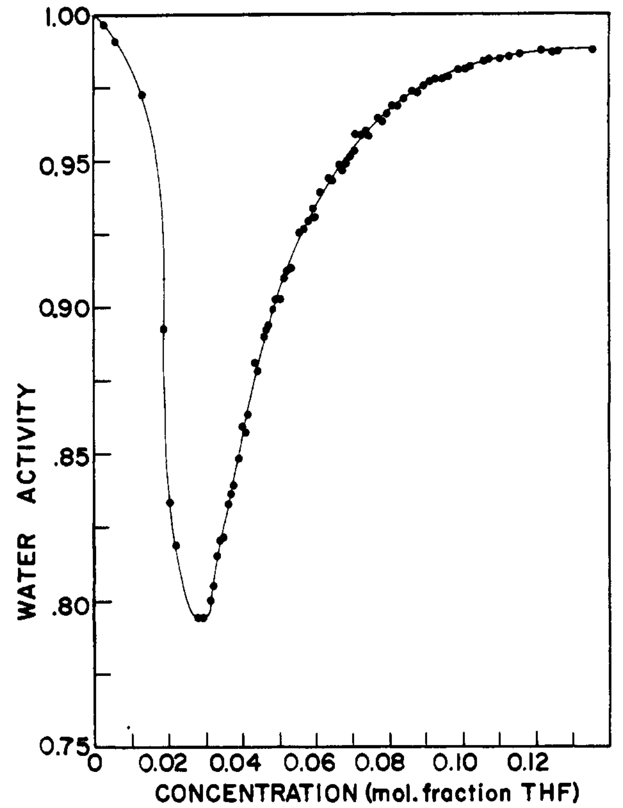

Figure 2. Expanded graph of activity of water at low THF concentrations

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 = activity of THF
a_2 = activity of water
t = temperature, °C
x_1 = liquid concentration, mole fraction THF
y_1 = vapor concentration, mole fraction THF
α_{12} = relative volatility THF/H_2O
α_{21} = relative volatility H_2O/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 Nonaqueous Solvents
I. Thermodynamics of Dye-Dye Interactions in CCl_4 and C_6H_6

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The thermodynamic parameters of the dimerization of 4, 4′,4′′,4′′′-tetraoctadecylsulfonamido copper(II) phthalocyanine in benzene and carbon tetrachloride were determined by an adiabatic calorimetric technique. The values for the dimerization in benzene were $\Delta H_1° = -10 \pm 1$ kcal/mol, $\Delta G_1° = -5.6 \pm 0.1$ kcal/mol, and $\Delta S_1° = -15 \pm 4$ 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 $\Delta H_1° \approx -13$ kcal/mol, $\Delta G_1° \approx -8.7$ kcal/mol, and $\Delta S_1° \approx -15$ 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′′′-tetraoctadecylsulfonamido 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(II) 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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