larger magnitude of the exothermic maximum in the present study compared to the dioxane-water system.

These results indicate strong hydrogen bonding between the ether and water. The endothermic region probably results from the breakup of the water network to form an ether-water network, with a net decrease in the number of hydrogen bonds. The strongly exothermic region probably results from ether entering the open network of water with a net increase in the number of hydrogen bonds. The maximum is larger than observed for the dioxane-water system, which may be because the open chain is able to enter the water network with less destruction of the water structure than occurs with dioxane. This is reflected by the large molal heat of solution at the low concentrations of diethylene glycol dimethyl ether in Table I.

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Power series equations describing the variation of the heat of solution in the various concentration units were obtained using computer facilities at the Oak Ridge National Laboratory and were used to obtain the extrapolated heat of solution noted in Table I, and to plot the curve in Figure 1. This part of the work was done while the first author was a participant in the Oak Ridge Associated Universities summer research program.

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Refractive Index and Dielectric Constant of Mixtures of Carbon Tetrachloride with Benzene, *p*-Xylene, and Mesitylene

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Measurements at 25° C of the refractive index at seven wavelengths and the low frequency dielectric constant are reported for mixtures of carbon tetrachloride with benzene, *p*-xylene, and mesitylene. Dispersion formulas have been obtained for the refractive index, and values of the molar refraction and molar polarization are also reported.

The presence of weak complexes in liquid mixtures of carbon tetrachloride with aromatic hydrocarbons has been inferred from measurements of heats of mixing (*3*) and spectra (*1*, *9*). Recently a method has been described (*2*) by which refractive index and dielectric constant data can be used to determine the properties of such weak complexes. The present measurements are part of a study of the applicability of this method.

EXPERIMENTAL

Details of the experimental methods have been previously reported (*2*). The refractive index measurements were performed by the method of minimum deviation. The divided circle on the spectrometer could be read to 30 sec of arc so that with the 60° prism-angle cell, the refractive index could be determined with an accuracy of 2×10^{-4}. Temperatures were measured with a Beckmann thermometer that was calibrated with a standard platinum thermometer. The temperature uncertainty of ±0.03° C leads to a maximum error of 2×10^{-5} in n.

Dielectric constants were measured at 1 kHz with a General Radio 1615-A capacitance bridge. Although the accuracy of the bridge allows measurements of the dielectric constant to be made to $\pm 1 \times 10^{-5}$, the precision of the dielectric constant measurements is 0.0001. This difference is the result of variations in stray capacitance with different fillings of the cell.

Mixtures were prepared by weight (*2*), and the uncertainties in mole fraction are ±0.0001. The benzene was material purified for the previous studies (*2*). Carbon tetrachloride (Matheson, Coleman and Bell, 99.98%), mesitylene (Matheson, Coleman and Bell, 99.98%), and *p*-xylene (Phillips Petroleum, 99.95%) were dried before use by distillation from over sodium but were not purified further.

RESULTS

In Table I, we compare our refractive index data for the pure substances at three wavelengths to some literature values. For benzene and *p*-xylene, the data agree within experimental error, but for mesitylene and carbon tetrachloride there are discrepancies that lie outside the overlap of estimated errors. The refractive index measurements for the mixtures are shown in Table II. The experimental refractive indices for each mixture have been fitted by least squares to a three-term Cauchy dispersion formula

$$n = n_\infty + a/\lambda^2 + b/\lambda^4$$

where λ is the wavelength. Values of the constants n_∞, a, and b are listed in Table III. The dispersion relations fit each set of data with a standard deviation no greater than 0.0002.

Results of the dielectric constant measurements are given in Table IV. For the pure liquids the good agreement

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Table I. Comparisons with Literature Values at 25.0° C

	Refractive index							
	5893 Å		5461 Å		4358 Å		Dielectric constant	
	Obsd[a]	Lit.[b]	Obsd[a]	Lit.[b]	Obsd[a]	Lit.[b]	Obsd[a]	Lit.[c]
CCl_4	1.4575	1.4573	1.4600	1.4596	1.4699	1.4693	2.228_8	2.228
C_6H_6	1.4981	1.4979	1.5020	1.5020	1.5199	1.5198	2.274_1	2.274
C_8H_{10}	1.4933	1.4933	1.4968	1.4971	1.5136	1.5137	2.261_2	2.262
C_9H_{12}	1.4973	1.4968	1.5009	1.5006	1.5173	1.5170	2.275_0	2.270

[a] Data have been corrected to 25.0° C using literature values of dn/dt and $d\epsilon/dt$. [b] Ref. *10.* [c] Ref. *4.*

Table II. Refractive Index Measurements

x_{CCl_4}	6213 Å	6010 Å	5893 Å	5845 Å	5649 Å	5461 Å	4358 Å
			CCl_4–C_6H_6, T = 24.83° C				
0.0000	1.4958	1.4974	1.4982	1.4982	1.5004	1.5021	1.5200
0.2924	1.4842	1.4857	1.4860	1.4867	1.4883	1.4899	1.5052
0.5538	1.4743	1.4755	1.4758	1.4763	1.4776	1.4788	1.4926
0.7727	1.4654	1.4664	1.4669	1.4673	1.4684	1.4697	1.4813
1.0000	1.4562	1.4570	1.4576	1.4578	1.4590	1.4601	1.4700
			CCl_4–C_8H_{10}, T = 24.85° C				
0.0000	1.4912	1.4926	1.4934	1.4938	1.4955	1.4969	1.5137
0.3377	1.4825	1.4837	1.4844	1.4851	1.4865	1.4880	1.5030
0.5390	1.4755	1.4765	1.4770	1.4775	1.4787	1.4804	1.4940
0.6925	1.4705	1.4715	1.4721	1.4725	1.4737	1.4750	1.4875
1.0000	1.4562	1.4570	1.4576	1.4578	1.4590	1.4601	1.4700
			CCl_4–C_9H_{12}, T = 24.83° C				
0.0000	1.4951	1.4965	1.4974	1.4978	1.4993	1.5010	1.5174
0.3794	1.4828	1.4840	1.4848	1.4851	1.4866	1.4882	1.5029
0.4344	1.4815	1.4828	1.4837	1.4838	1.4853	1.4871	1.5016
0.6839	1.4710	1.4721	1.4725	1.4731	1.4745	1.4756	1.4883
1.0000	1.4562	1.4570	1.4576	1.4578	1.4590	1.4601	1.4700

Table III. Constants for Dispersion Equation and Molar Refraction at 5893 Å

x_{CCl_4}	n_∞	$a \times 10^{-5}$, Å^{-2}	$b \times 10^{-12}$, Å^{-4}	$\tilde{V}$, cm^3/mol	R_M, cm^3/mol
		CCl_4–C_6H_6			
0.0000	1.4779	5.93	3.9	89.39	26.21
0.2924	1.4669	6.15	2.1	91.64	26.31
0.5538	1.4628	3.07	4.8	93.65	26.40
0.7727	1.4523	4.59	1.7	95.33	26.45
1.0000	1.4427	5.15	0.0	97.07	26.47
		CCl_4–C_8H_{10}			
0.0000	1.4753	5.08	4.2	123.92	36.04
0.3377	1.4651	6.23	1.8	114.83	32.88
0.5390	1.4617	4.48	3.2	109.44	30.92
0.6925	1.4571	4.59	2.3	105.31	29.49
1.0000	1.4427	5.15	0.0	97.07	26.47
		CCl_4–C_9H_{12}			
0.0000	1.4779	5.88	3.1	139.58	40.87
0.3794	1.4664	5.71	2.3	123.79	35.48
0.4344	1.4641	6.32	1.5	121.47	34.74
0.6839	1.4563	5.24	1.6	111.02	31.12
1.0000	1.4427	5.15	0.0	97.07	26.47

Table IV. Dielectric Constant Measurements

x_{CCl_4}	ϵ	$\tilde{V}$, cm^3/mol	P_M, cm^3/mol
	CCl_4–C_6H_6, T = 25.4° C		
0.0000	2.2733_4	89.45	26.66
0.2470	2.2659_5	91.36	27.11
0.5050	2.2543_0	93.34	27.52
0.7539	2.2422_1	95.25	27.89
1.0000	2.2284_7	97.13	28.22
	CCl_4–C_8H_{10}, T = 25.0° C		
0.0000	2.2612_2	123.92	36.68
0.2492	2.2609_6	117.23	34.69
0.5026	2.2534_0	110.42	32.54
0.7542	2.2436_0	103.67	30.38
1.0000	2.2287_7	97.09	28.21
	CCl_4–C_9H_{12}, T = 25.0° C		
0.0000	2.2749_5	139.59	41.63
0.2485	2.2661_0	129.41	38.37
0.5020	2.2561_4	118.68	35.01
0.7482	2.2440_3	108.08	31.68
1.0000	2.2288_5	97.09	28.21

between our data and the literature values is shown in Table I.

The molar refraction at 5893 Å and the molar polarization have been calculated from our data. They are listed in Tables III and IV. Molar volumes for the *p*-xylene and mesitylene mixtures have been obtained by combining the molar volumes of the pure components (*8*) with excess volumes. Measurements of V^e, the excess volume, were performed for equimolar mixtures with a dilatometer of the type described by McLure and Swinton (*5*). At 25° C, V^e (x = ½) is 0.01 cm^3/mol for CCl_4–C_8H_{10} and 0.35 cm^3/mol for CCl_4–C_9H_{12}. Values of V^e at other concentrations were calculated assuming the parabolic concentration dependence that is a good approximation for many simple mixtures (*6*). Since V^e is small for these mixtures, the error in assuming the parabolic dependence is probably negligible. The excess volume for CCl_4–C_6H_6 at 25° C is negligibly small (*7*).

For carbon tetrachloride-benzene, both the molar refraction and molar polarization show small positive deviations from additivity; the mixtures with *p*-xylene and mesitylene display additive behavior. These small deviations suggest that the complexes formed have dipole moments <0.2 D (*2*).

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Mutual Solubilities of Propylene Carbonate and Water

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The complete liquid-liquid phase diagram at atmospheric pressure has been measured for propylene carbonate–water. The upper critical solution temperature is 61.1° C at a mole fraction of propylene carbonate x = 0.575.

As part of a study of some solvents of interest in natural gas processing, we have investigated the phase diagram of the system propylene carbonate-water. The complete liquid-liquid region was studied, and measurements were made over most of the solid-liquid region, although the eutectic temperature was not determined precisely.

Measurements were made using laboratory distilled water and Koch Light "puriss"-grade propylene carbonate of purity >99%. The latter material was dried over a Linde molecular sieve, grade 5A.

At temperatures above 0° C, observations were made using the cloud-point method (*4*). Mixtures were prepared by weight in pyrex tubes of 5-mm internal diameter. The sealed tubes were immersed in a water bath at a temperature above the unmixing temperature and cooled at about 0.5° C min^{-1}. The cloud-point temperatures were measured with a mercury-in-glass thermometer. The temperatures recorded are the means of several observations on each mixture and are believed to be accurate to ±0.1° C.

The low-temperature measurements were taken from cooling curves (*2*) measured on mixtures prepared by weight in 25 cc test tubes and cooled slowly by a dry ice-acetone bath. Temperatures were measured with a thallium amalgam thermometer and are believed to be accurate to ±0.2° C. Temperatures listed in Table I for this region are those of the discontinuities in the temperature time curves. The results are also shown in Figure 1, along with the data of Marsden (*3*) and Doolittle (*1*), the only other solubility data we were able to find.

A small degree of hydrolysis of propylene carbonate was indicated by repeated measurements over a long period.

Table I. Phase Separation Temperatures for Propylene Carbonate–Water at Atmospheric Pressure

Wt fraction, propylene carbonate	Mole fraction, propylene carbonate	t/° C
0	0	0
0.050	0.0092	−0.6
0.100	0.0192	1.5
0.175	0.0361	25.0
0.196	0.0412	30.1
0.354	0.0882	52.1
0.478	0.1391	59.7
0.575	0.1926	61.1
0.740	0.3343	56.1
0.850	0.5000	41.6
0.930	0.7010	25.0
0.946	0.7556	20.1
0.975	0.8732	−15.5
0.990	0.9458	−30.1
1.000	1.0000	−55.2[a]

[a] From Marsden (*3*).

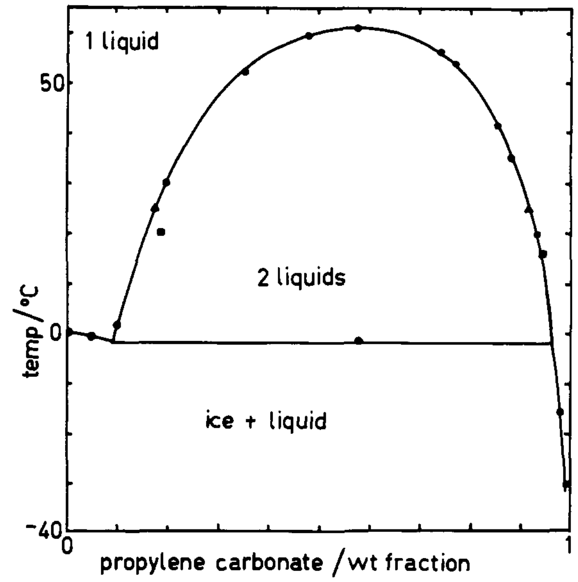

Figure 1. Phase diagram for propylene carbonate–water system at 1-atm pressure
● This work. ▲ Ref. 3. ■ Ref. 1

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