ACKNOWLEDGMENT

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NOMENCLATURE

a = Activity
A = Limit of log γ as $x \to 0$ in a binary solution
x = Mole fraction, based on acetic acid molecular weight of 120.1
X = Weight fraction
γ = Activity coefficient

SUBSCRIPTS

A = Ethyl acetate, component or phase
B = Ethylene glycol, component or phase
C = Acetic acid

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Dielectric Behavior of Some Alcohol and Carbon Tetrachloride Mixtures

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Dielectric constant data are presented for a number of alcohol and carbon tetrachloride mixtures obtained at 22°, 30°, and 40° C. Densities and the Fröhlich correlation parameter also are included.

A NUMBER of progressively more detailed theories have been developed to describe the dielectric behavior of fluids whose molecules possess a permanent dipole moment. The simplest theories, those of Clausius-Mosotti and Debye (*7*), neglect intermolecular forces. These yield satisfactory results only for gases at low pressures.

The Onsager theory (*13*) recognizes that when a molecule having a permanent dipole moment is surrounded by other molecules, the field of the dipole polarizes the surrounding molecules, since they have a polarizability, even if no permanent moment. This polarization of the environment of a molecule gives rise to a field at the location of the molecule. The theory is limited by the assumption that the molecule occupies a spherical cavity in the dielectric. A more limiting factor is the treatment of the entire surroundings of each molecule as a homogeneous continuum, making no distinction between interactions of closely neighboring molecules and those relatively far apart. Just this distinction is needed for an effective treatment of associated liquids.

By using classical statistical mechanics, Fröhlich (*8, 9*) showed that the dielectric constant of a fluid can be related to the dipole moment of a free molecule of the fluid by the equation

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon}\frac{M}{d} = \frac{n_*^2 - 1}{n_*^2 + 2}\frac{M}{d}\left[\frac{(n_*^2 + 2)(2\epsilon + 1)}{(n_*^2 + 2\epsilon)}\right] + \frac{4\pi N_A}{3}\frac{g\mu_0^2}{9kT}\left[\frac{(n_*^2 + 2)(2\epsilon + 1)}{(n_*^2 + 2\epsilon)}\right]^2 \qquad (1)$$

where ϵ is the dielectric constant, M the molecular weight, d the density in grams per cm.^{3}, and n_* the refractive index of the fluid. μ_0 is the dipole moment of a free molecule, N_A is Avogadro's number, and k is the Boltzmann constant. n_* refers to the refractive index measured at frequencies high enough so that orientational polarization effectively has ceased.

The parameter g represents the influence of hindered molecular rotation due to close range intermolecular forces such as occur in liquids which exhibit hydrogen bonding. g is called the correlation parameter. It is defined by the expression

$$g = [1 + n\,\overline{\cos\gamma}] \qquad (2)$$

where n is the number of molecules in a sphere of the fluid surrounding a molecule with dipole moment μ and $\overline{\cos\gamma}$ is the average value of the cosine of the angle between the dipole moments of an arbitrary pair of dipoles. Clearly, in the absence of specific close range interactions—such as hydrogen bonding—$\overline{\cos\gamma} = 0$. In this limit, the Fröhlich equation is identical to that of Onsager.

The Fröhlich equation can be extended to consider the case of binary mixtures of polar liquids in nonpolar solvents.

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{3\epsilon}\frac{M}{d} = \left[\frac{(n_*^2)_1 - 1}{(n_*^2)_1 + 2}\cdot\frac{M_1}{d_1}\right] \times \left[\frac{\{(n_*^2)_1 + 2\}\{2\epsilon + 1\}}{\{(n_*^2)_1 + 2\epsilon\}}\right]x_1 + \left[\frac{(n_*^2)_2 - 1}{(n_*^2)_2 + 2}\cdot\frac{M_2}{d_2}\right]\left[\frac{\{(n_*^2)_2 + 2\}\{2\epsilon + 1\}}{\{(n_*^2)_2 + 2\epsilon\}}\right]x_2 + \frac{4\pi N_A}{3}\frac{g(\mu_0^2)_1}{9kT}\left[\frac{\{(n_*^2)_1 + 2\}\{2\epsilon + 1\}}{\{(n_*^2)_1 + 2\epsilon\}}\right]^2 x_1 \qquad (3)$$

where x_1 and x_2 are the mole fractions of the polar and nonpolar components, respectively.

EQUIPMENT AND PROCEDURE

Dielectric constant measurements were carried out by the substitution method using a Schering-type capacitance bridge at a frequency of one megacycle. A Boonton Radio Corp. RX meter Type 250-A was used as a bridge. This instrument is completely self-contained, consisting of an oscillator, detector, amplifier, null detector, and power supply, in addition to the bridge circuit. The specially constructed cylindrical test cell was connected into the bridge circuit in parallel with a General Radio Corp. Type 1422-N precision capacitor. The cell constant for the apparatus was determined from comparison of capacitance values with the test cell empty and filled with a calibrating liquid of known dielectric constant. The same procedure used for calibration was then repeated substituting the unknown alcohol–carbon tetrachloride mixtures for the calibrating liquid at three different temperatures. Each measurement of the dielectric constant was repeated at least twice with different samples of the same unknown to ensure the reproducibility of the results.

The temperature was controlled to ±0.01° C. by immersing the cell in a Fisher No. 15-452 Isotemp constant temperature bath, and the temperature checked with a National Bureau of Standards calibrated thermometer with an accuracy of about ±0.05° C.

The density of each mixture was determined according to standard methods (*2*), using 25-ml. pycnometers with expansion caps to minimize evaporation losses. The pycnometers were calibrated with distilled water.

Owing to the fact that in all cases at least one of the components was highly volatile, special care was exercised to avoid excessive evaporation during handling. As a matter of caution, all transfers of liquid were made using hypodermic syringes, and the test cell was sealed tightly during each measurement.

Test Cells. Two stainless steel test cells were constructed to cover the entire range of dielectric constants of the liquids considered. These test cells and their important dimensions are shown in cross-section in Figures 1 and 2.

The "low" cell had a volume of about 17 ml. and an empty capacitance of about 105 p.f. This cell was used to measure dielectric constants up to 12.0. The "high" cell was about 7 ml. in volume with an empty capacitance of about 22 p.f., and was used for mixtures with dielectric constants higher than 12.0.

Calibrating Liquids. All of the dielectric constants obtained in this work are based on the use of benzene and chlorobenzene as calibration standards. The dielectric constants and their temperature coefficient for benzene and chlorobenzene have been tabulated by the National Bureau of Standards (*12*) with a probable accuracy of about 0.1%. These values are:

Benzene	Chlorobenzene
$(\epsilon)_{20^\circ \text{ C.}} = 2.284$	$(\epsilon)_{20^\circ \text{ C.}} = 5.708$
$(\epsilon)_{25^\circ \text{ C.}} = 2.274$	$(\epsilon)_{25^\circ \text{ C.}} = 5.621$
$(\epsilon)_{t'^\circ \text{ C.}} = (\epsilon)_{t^\circ \text{C}} - 0.0020(t' - t)$	$\log(\epsilon)_{t'^\circ \text{ C.}} = \log_{10}(\epsilon)_{t^\circ \text{ C}} - 0.00133(t' - t)$

where *t* and *t'* are temperatures in degrees centigrade.

The cell constant for the low cell was determined by comparing the capacitance values measured with the cell evacuated and filled with benzene. The calibration thus obtained was then checked for accuracy by repeating the procedure with chlorobenzene.

The high cell was calibrated in a like manner using chlorobenzene. In this case, the pure alcohols were used as a check for the upper limits.

Materials. Since the dielectric constant is sensitive to impurities, the substances obtained were of the highest quality commercially available. In all cases, only those substances were considered for which stated purity was in excess of 99.5% by weight.

As a further check on the suitability of the materials used, the dielectric constants of the pure liquids obtained were compared with values published by the NBS (*12*) and others (*1, 5, 10, 14*). In most cases, the agreement was within the accuracy assigned to the NBS values, and in all cases, agreement was within the accuracy assigned to the values obtained here.

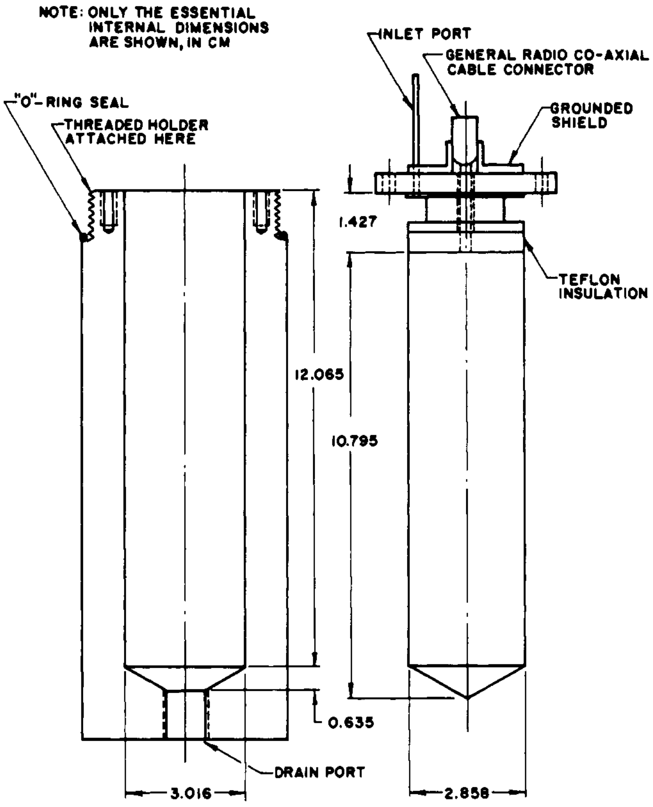

Figure 1. "Low" cell

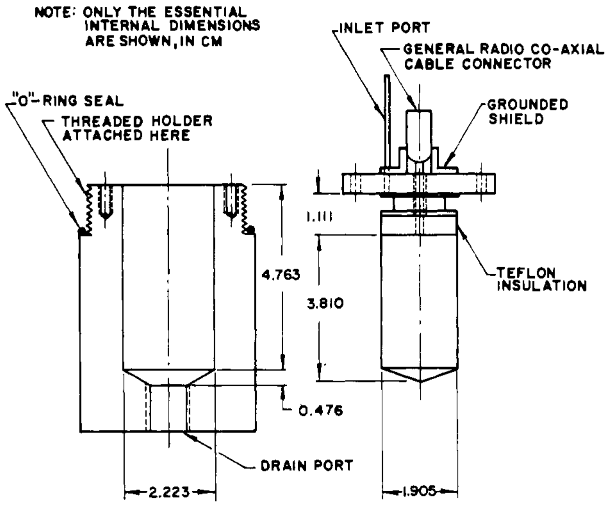

Figure 2. "High" cell

Table I. Experimental Results

	22.0° C.			30.0° C.			40.0° C.		
Mole Fraction of Alcohol, x_A	Dielectric constant, ϵ	Density, g./cc. d	Correlation parameter, g	Dielectric constant, ϵ	Density, g./cc. d	Correlation parameter, g	Dielectric constant, ϵ	Density, g./cc. d	Correlation Parameter, g
				$CH_3OH + CCl_4$					
0.0	2.232[a]	1.592	1.0	2.216	1.577	1.0	2.196	1.558	1.0
0.0104	2.267	1.591	0.923	2.249	1.575	0.935	...	...	...
0.0118	2.272	1.590	0.949	2.255	1.575	0.966	...	...	...
0.0215	2.301	1.587	0.906	2.284	1.572	0.932	...	...	...
0.0608	2.433	1.570	0.933	2.417	1.555	0.974	2.393	1.536	1.007
0.1030	2.635	1.556	1.043	2.612	1.540	1.074	2.576	1.521	1.089
0.1683	3.126	1.530	1.300	3.071	1.515	1.303	3.003	1.496	1.301
0.1982	3.426	1.517	1.418	3.348	1.503	1.407	3.258	1.484	1.398
0.3022	4.88	1.470	1.798	4.707	1.455	1.775	4.489	1.437	1.733
0.4057	7.03	1.414	2.145	6.682	1.400	2.095	6.313	1.383	2.045
1.0	33.4[a]	0.790	2.835	32.1	0.783	2.835	29.92	0.773	2.773
				$n\text{-}C_3H_7OH + CCl_4$					
0.0[c]	2.233	1.594	1.0	2.217	1.578	1.0	2.197	1.558	1.0
0.0350	2.336	1.572	0.857	2.320	1.556	0.897	2.302	1.537	0.957
0.0499	2.374	1.560	0.833	2.361	1.546	0.876	2.346	1.527	0.951
0.1087	2.569	1.524	0.863	2.552	1.509	0.897	2.530	1.491	0.938
0.1557	2.811	1.492	0.998	2.782	1.479	1.017	2.743	1.460	1.039
0.2026	3.152	1.462	1.162	3.094	1.448	1.161	3.02	1.430	1.156
0.4171	6.37	1.313	2.088	5.978	1.300	1.998	5.526	1.284	1.889
0.6178	11.3	1.156	2.752	10.5	1.145	2.637	9.7	1.132	2.538
0.8112	16.0	0.987	2.950	15.0	0.979	2.861	13.8	0.968	2.755
1.0[a]	20.5	0.804	2.972	19.3	0.797	2.903	18.2	0.789	2.873
				$iso\text{-}C_3H_7OH + CCl_4$					
0.0[b]	2.233	1.593	1.0	2.217	1.577	1.0	2.197	1.558	1.0
0.0452	2.358	1.563	0.782	2.344	1.547	0.831	2.328	1.527	0.913
0.0506	2.367	1.559	0.750	2.355	1.543	0.807	2.338	1.523	0.879
0.0972	2.495	1.527	0.744	2.484	1.512	0.790	2.470	1.493	0.854
0.0973	2.488	1.527	0.725	2.476	1.511	0.770	2.465	1.493	0.838
0.1368	2.623	1.499	0.770	2.607	1.485	0.801	2.591	1.466	0.856
0.1469	2.668	1.493	0.791	2.656	1.478	0.833	2.642	1.460	0.890
0.1866	2.848	1.465	0.857	2.821	1.450	0.880	2.790	1.432	0.913
0.1901	2.878	1.462	0.873	2.854	1.448	0.905	2.826	1.430	0.945
0.2745	3.434	1.403	1.098	3.426	1.389	1.110	3.34	1.372	1.113
0.3096	3.832	1.377	1.208	3.690	1.363	1.170	3.554	1.346	1.147
0.3605	4.481	1.341	1.363	4.220	1.328	1.307	4.04	1.312	1.279
0.3765	4.706	1.329	1.445	4.519	1.315	1.415	4.29	1.298	1.372
0.4469	5.886	1.276	1.701	5.609	1.262	1.661	5.24	1.245	1.593
1.0[c]	20.1	0.784	2.885	18.7	0.778	2.778	17.2	0.770	2.675
				$n\text{-}C_4H_9OH + CCl_4$					
0.0[a]	2.234	1.593	1.0	2.218	1.577	1.0	2.198	1.558	1.0
0.0397	2.346	1.561	0.834	2.332	1.546	0.880	2.317	1.531	0.937
0.0873	2.475	1.526	0.790	2.461	1.512	0.826	2.448	1.496	0.887
0.1463	2.697	1.484	0.870	2.678	1.470	0.900	2.662	1.145	0.961
0.2058	3.040	1.437	1.042	2.991	1.425	1.040	2.947	1.410	1.061
0.2884	3.786	1.374	1.347	3.656	1.363	1.306	3.528	1.350	1.776
0.4161	5.706	1.275	1.916	5.349	1.265	1.814	4.974	1.256	1.704
0.6182	10.11	1.120	2.678	9.349	1.110	2.544	8.498	1.098	2.392
1.0[d]	18.1	0.810	3.129	17.0	0.804	3.042	15.7	0.796	2.939
				$iso\text{-}C_4H_9OH + CCl_4$					
0.0[a]	2.232	1.593	1.0	2.216	1.577	1.0	2.196	1.558	1.0
0.0231	2.299	1.574	0.872	2.285	1.561	0.900	2.265	1.544	0.925
0.0509	2.364	1.554	0.759	2.351	1.537	0.819	2.336	1.518	0.897
0.1064	2.513	1.510	0.761	2.502	1.495	0.807	2.489	1.477	0.871
0.1540	2.592	1.474	0.838	2.673	1.460	0.867	2.652	1.441	0.916
0.2214	3.065	1.421	1.014	3.018	1.409	1.017	2.963	1.390	1.034
0.3198	3.999	1.345	1.386	3.831	1.334	1.328	3.663	1.316	1.289
0.4102	5.370	1.275	1.802	5.014	1.263	1.694	4.639	1.248	1.582
0.6162	9.797	1.113	2.642	9.012	1.103	2.492	8.10	1.090	2.311
1.0[a]	18.3	0.802	3.237	17.0	0.795	3.114	15.7	0.787	3.009
				$sec\text{-}C_4H_9OH + CCl_4$					
0.0[a]	2.234	1.593	1.0	2.218	1.577	1.0	2.198	1.558	1.0
0.0395	2.348	1.561	0.852	2.335	1.544	0.922	...	...	...

(Continued on page 7)

Table I. (*Continued*)

	22.0° C.			30.0° C.			40.0° C.		
Mole Fraction of Alcohol, x_A	Dielectric constant, ϵ	Density, g./cc. d	Correlation parameter, g	Dielectric constant, ϵ	Density, g./cc. d	Correlation parameter, g	Dielectric constant, ϵ	Density, g./cc. d	Correlation parameter, g
sec-$C_4H_9OH + CCl_4$, cont'd									
0.0994	2.489	1.516	0.735	2.480	1.500	0.790	2.471	1.481	0.869
0.1588	2.663	1.469	0.758	2.655	1.455	0.803	2.642	1.438	0.858
0.2015	2.825	1.437	0.804	2.809	1.423	0.838	2.790	1.405	0.887
0.3090	3.435	1.350	1.010	3.368	1.341	1.005	3.293	1.324	1.016
0.4064	4.377	1.279	1.279	4.175	1.266	1.230	3.980	1.251	1.192
0.7069	10.06	1.044	2.332	9.144	1.034	2.172	8.127	1.021	1.989
1.0[d]	17.3	0.806	2.995	15.9	0.799	2.846	14.2	0.791	2.649
n-$C_5H_{11}OH + CCl_4$									
0.0[a]	2.231	1.593	1.0	2.215	1.577	1.0	2.195	1.558	1.0
0.0275	2.811	1.566	0.882	2.299	1.555	0.912	...	...	...
0.0533	2.370	1.545	0.770	2.361	1.530	0.839	2.347	1.512	0.915
0.1044	2.491	1.505	0.752	2.484	1.491	0.806	2.470	1.474	0.863
0.1520	2.669	1.461	0.823	2.654	1.447	0.859	2.637	1.430	0.908
0.2081	2.935	1.414	0.944	2.903	1.401	0.962	2.868	1.384	0.991
0.3132	3.750	1.328	1.284	3.631	1.316	1.254	3.508	1.301	1.230
0.4116	5.144	1.244	1.786	4.827	1.233	1.686	4.528	1.220	1.598
0.6924	10.35	1.035	2.760	9.50	1.027	2.596	8.64	1.016	2.434
1.0	15.5	0.814	3.128	14.6	0.808	3.046	13.5	0.801	2.926
iso-$C_5H_{11}OH + CCl_4$									
0.0[a]	2.234	1.593	1.0	2.218	1.577	1.0	2.198	1.558	1.0
0.0372	2.334	1.558	0.813	2.320	1.543	0.860	2.303	1.526	0.916
0.1061	2.501	1.499	0.741	2.491	1.485	0.786	2.479	1.468	0.847
0.1603	2.674	1.452	0.797	2.664	1.441	0.833	2.646	1.426	0.874
0.2133	2.908	1.406	0.904	2.884	1.397	0.919	2.855	1.386	0.942
0.3070	3.546	1.330	1.164	3.467	1.320	1.154	3.370	1.307	1.140
0.4269	4.952	1.233	1.637	4.693	1.224	1.563	4.415	1.213	1.481
0.7656	11.5	0.976	2.895	10.64	0.968	2.756	9.633	0.958	2.576
1.0[f]	15.6	0.809	3.208	14.6	0.802	3.107	13.4	0.794	2.964
tert-$C_5H_{11}OH + CCl_4$									
0.0[a]	2.234	1.593	1.0	2.218	1.577	1.0	2.198	1.558	1.0
0.0457	2.363	1.553	0.819	2.350	1.537	0.877	2.330	1.519	0.920
0.1050	2.480	1.501	0.679	2.475	1.485	0.742	2.467	1.464	0.827
0.1624	2.570	1.457	0.588	2.572	1.442	0.646	2.569	1.422	0.717
0.2146	2.679	1.406	0.601	2.689	1.393	0.658	2.693	1.376	0.726
0.2906	2.821	1.341	0.585	2.840	1.329	0.641	2.854	1.313	0.708
0.4178	3.085	1.240	0.581	3.119	1.228	0.638	3.140	1.212	0.700
0.7677	4.302	1.099	0.589	4.270	1.090	0.608	4.237	1.076	0.637
1.0[a]	6.201	0.807	1.044	5.849	0.803	0.998	5.532	0.798	0.963
n-$C_7H_{15}OH + CCl_4$									
0.0[a]	2.234	1.593	1.0	2.218	1.577	1.0	2.198	1.558	1.0
0.0391	2.340	1.549	0.774	2.328	1.533	0.842	2.308	1.515	0.883
0.1005	2.480	1.484	0.701	2.473	1.469	0.759	2.460	1.452	0.818
0.1514	2.619	1.433	0.731	2.609	1.419	0.774	2.595	1.403	0.824
0.2189	2.865	1.367	0.836	2.846	1.353	0.869	2.818	1.339	0.898
0.3014	3.278	1.293	1.004	3.225	1.281	1.011	3.169	1.268	1.023
0.3392	3.544	1.261	1.115	3.455	1.250	1.100	3.369	1.239	1.091
0.7562	8.76	0.961	2.499	8.12	0.954	2.367	7.31	0.945	2.173
1.0[a]	11.5	0.821	2.834	10.7	0.815	2.712	9.74	0.808	2.544
n-$C_8H_{17}OH + CCl_4$									
0.0	2.234	1.593	1.0	2.218	1.577	1.0	2.198	1.557	1.0
0.0413	2.343	1.542	0.794	...	...	...	2.312	1.513	0.879
0.0473	2.353	1.533	0.772	2.340	1.520	0.808	2.324	1.501	0.889
0.1014	2.408	1.472	0.712	2.461	1.459	0.763	2.451	1.441	0.840
0.1515	2.596	1.417	0.748	2.589	1.405	0.793	2.579	1.388	0.857
0.1923	2.718	1.375	0.795	2.708	1.363	0.835	2.696	1.348	0.889
0.2976	3.163	1.277	0.995	3.126	1.266	1.012	3.077	1.252	1.031
0.4048	3.881	1.188	1.299	3.758	1.177	1.273	3.626	1.166	1.244
0.7095	7.256	0.978	2.332	6.734	0.971	2.200	6.149	0.963	2.038
1.0	10.22	0.826	2.843	9.614	0.820	2.752	8.725	0.813	2.566

[a] See reference (*12*).

[b] See reference (*6*).

[c] See reference (*7*).

[d] See reference (*5*)

[e] See reference (*1*).

[f] See reference (*14*).

Estimated Accuracy of Results. The General Radio Corp. 1422-N capacitor used in these studies was accompanied by a precision calibration curve, so that the capacitance differences measured on this instrument were accurate to ±0.2 p.f. or ±0.03%, whichever was the greater.

The values of the dielectric constant recorded in Table I have an estimated accuracy determined by the number of figures retained.

Values listed to four figures are considered accurate to 0.5%.

Values listed to three figures are considered accurate to 2%.

Values listed to two figures are considered less accurate than to 2%.

Samples usually were prepared in lots of about 125 ml. to provide for at least two readings at each temperature, and were weighed to an accuracy of ±0.02 gram. Consequently, values of the mole fractions given probably are good to about 1% for the more alcohol-rich mixtures. For more dilute mixtures, this accuracy is somewhat less than 1%.

Density measurements were performed on smaller samples, such as 25 ml., and an analytical balance was used in all weighings. Therefore, it is estimated that the reported density measurements are accurate to better than 1%.

EXPERIMENTAL RESULTS

The experimental results are summarized in Tables I and II. Included are: experimentally determined dielectric constants and densities at 22°, 30°, and 40° C; the correlation parameter, g, calculated from Equation 3; and appropriate molecular parameters.

With one exception, all of the substances measured show the same general behavior of g. For the pure alcohols, g is large, approximately 2.5–3.1, indicating a high degree of mutual coordination. As the alcohol concentration decreases, g decreases to a minimum value, less than one, and then increases towards one with further dilution. The fact that g is less than one for dilute solutions indicates that in this concentration region an appreciable number of alcohol complexes are formed in which the dipoles are oriented in an antiparallel fashion.

Table II. Molecular Parameters

Material	μ_0, (Debye Units)	n_*^2, ° C.		
		22	30	40
CH_3OH	1.70 (*11*)	1.94 (*4*)	1.93 (*4*)	1.92 (*4*)
C_3H_7OH	1.67 (*11*)	2.11 (*6*)	2.10 (*6*)	2.08 (*6*)
iso-C_3H_7OH	1.66 (*11, 15, 16*)	2.20 (*10*)	2.19 (*10*)	2.17 (*10*)
C_4H_9OH	1.65 (*11*)	2.19[a]	2.18[a]	2.16[a]
iso-C_4H_9OH	1.64 (*11*)	2.19[a]	2.18[a]	2.16[a]
sec-C_4H_9OH	1.65 (*16*)	2.19[a]	2.18[a]	2.16[a]
$C_5H_{11}OH$	1.65 (*16*)	2.19[a]	2.18[a]	2.17[a]
iso-$C_5H_{11}OH$	1.64 (*16*)	2.19[a]	2.18[a]	2.17[a]
tert-$C_5H_{11}OH$	1.65 (*16*)	2.19[a]	2.18[a]	2.17[a]
$C_7H_{15}OH$	1.64 (*3*)	2.27 (*3*)	2.26 (*3*)	2.25 (*3*)
$C_8H_{17}OH$	1.64 (*16, 3*)	2.21 (*3*)	2.20 (*3*)	2.19 (*3*)
CCl_4	0	2.234	2.218	2.198

[a] Estimated from data presented in references (*3, 4, 6,* and *10*).

The behavior of the correlation parameter of *tert*-pentanol is different from the other examples, and illustrates the effect of strong steric hindrance. For pure *tert*-pentanol, the correlation parameter is close to one indicating that coordination into chain-like complexes is approximately balanced by coordination into cyclic complexes. This is further confirmed by the generally lower values of g at all concentrations.

The effect of lowering the temperature is to enhance the coordination of the molecules in the pure alcohols, hence the correlation parameter increases. On the other hand, lowering the temperature also increases the stability of any associated structure. Thus, in the dilute solution region in which many complexes have a configuration with low dipole moment ($g < 1$), the correlation parameter decreases with temperature.

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