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Density and Relative Permittivity for 1-Alkanols + Dodecane at 298.15 K

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Densities and relative permittivities at a frequency of 30 kHz for the binary mixtures of 1-alkanols, $C_nH_{2n+1}OH$ for $n = 1$ to 10, + dodecane were measured for the mole fraction range of 1-alkanol between 0 and 0.1 at a temperature of 298.15 K. By using Debye and Frohlich equations, the apparent dipole moments (μ) of 1-alkanols were calculated, and the limiting values (μ_0) were determined by extrapolating to infinite dilution. The value of μ_0 decreased with increasing hydrocarbon length of the 1-alkanol. The present results were compared with our previous measurements in cyclohexane and heptane. Methanol had the same μ_0 value irrespective of solvent, while μ_0 for 1-alkanols with $n \geq 2$ showed a lower value in dodecane than those found in cyclohexane and heptane. The excess partial molar volumes of 1-alkanols at infinite dilution decreased with increasing n.

Introduction

The dipole moment (μ) is one of the very important properties of molecules because it is related to the molecular configuration as well as its polarity. It has been determined for many molecules by means of permittivity measurements since 1930.[1] However, the values of μ accumulated in the literature show large discrepancies except the most recent ones determined by using successive dilution methods developed for solutions.[2,3] Previous publications from our laboratory have reported apparent dipole moment of 1-alkanols, $C_nH_{2n+1}OH$ for $n = 1$ to 10, in cyclohexane and heptane, and excess molar volumes (V_m^E) for binary mixtures of those 1-alkanols + cyclohexane and heptane.[4] We found that the dipole moment of isolated alkanols (μ_0) determined by extrapolating to infinite dilution decreased with increasing n of the 1-alkanols. We also found a small but systematic effect on μ due to solvent. Thereby, we expected that the μ_0 of alkanols changes with the length of hydrocarbon used for a solvent. As an extension of our previous work the apparent dipole moments (μ) of $C_nH_{2n+1}OH$ for $n = 1$ to 10 were determined in dodecane. We also measured the densities (ρ) of those mixtures for the mole fraction (x) of alkanol for $x < 0.1$ at a temperature (T) of 298.15 K.

Experimental Section

Materials. The samples of 1-alkanol were the same as used in the previous work.[4] Dodecane was Cica-special grade reagent supplied from Kanto Chemical Co. Inc. and used as received. Other liquids were purified by distillation. Their purities were tested by GLC analysis, and the mole fraction of water in the used samples was measured by Karl Fischer method. The purified liquids were kept in sealed glass ampules after replacing the atmosphere with N_2 and stored in a refrigerator. The purities and the densities of the component liquids are listed in Table 1 along with literature values of refractive indices (n_D). The purification and the test of purity have been described in detail in the previous report.[4]

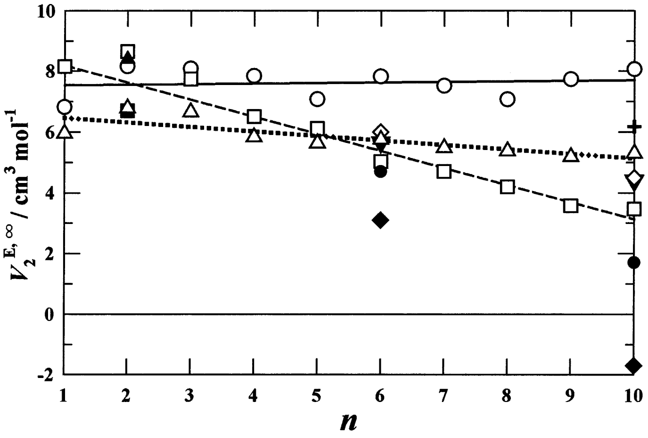

Figure 1. Excess partial molar volumes at the infinite dilution ($V_2^{E,\infty}$) for $C_nH_{2n+1}OH$ at 298.15 K. Our results: ○, in cyclohexane;[4] △, in dodecane; □, in heptane;[4] solid line, least squares representation in cyclohexane; broken line, least squares representation in heptane; doted line, least squares representation in dodecane. Literature values: ◆, in pentane;[13,14] ●, in hexane;[13,14] ▲, in hexane;[15] ▼, in octane;[13,14] ◇, in decane;[13,14] +, in hexadecane;[14] ■, in hexadecane.[23]

Measurements. The densities of {x1-alkanol + (1 − x)dodecane} were measured using a vibrating tube densimeter (Anton Paar, DMA-602). The temperature in the jacket of densimeter was controlled with water circulated with a temperature controller (CT-L, Sodev, Canada). It was stable within ± 0.0003 K for a period to measure several points accompanying a drift of 7×10^{-4} K during ordinary operation period of 3 h. The resonance period showed a drift of 0.0003 μs during the operation of 3 h. This drift corresponded to a shift of 4×10^{-7} g·cm^{-3} in density. The densimeter was calibrated by using the densities of heptane, cyclohexane, toluene, benzene, and chlorobenzene. The densities of these liquids were determined by use of a 50 cm^3 pycnometer with an uncertainty of $\pm 3 \times 10^{-6}$ g·cm^{-3}, and the vibrating tube densimeter

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Table 1. Densities (ρ) and Refractive Indices (n_D) at 298.15 K and Purities for the Component Liquids

componet liquid	purity/%[a]	$x(H_2O) \times 10^4$ [b]	ρ(obs)/g·cm^{-3}	ρ(lit)/g·cm^{-3}	ρ(lit)/g·cm^{-3}	n_D
dodecane	99.96	2.7	0.745435	0.74518[c]		
methanol	99.99	1.5	0.786538	0.78667[d]	0.78718[h]	1.32661[d]
ethanol	99.98	2.4	0.785055	0.78512[d]	0.78524[h]	1.35937[d]
1-propanol	99.99	3.4	0.799564	0.79960[c]	0.79976[h]	1.38348[d]
1-butanol	99.99	10.0	0.805767	0.80575[c]	0.80583[h]	1.39730[d]
1-pentanol	99.80	7.0	0.810883	0.81119[e]	0.81105[h]	1.40790[e]
1-hexanol	99.95	1.0	0.815275	0.81534[c]	0.81551[h]	1.41624[e]
1-heptanol	99.98	4.7	0.818746		0.81897[h]	1.4231[f]
1-octanol	99.97	5.5	0.821694	0.82177[e]	0.82180[h]	1.42757[e]
1-nonanol	99.21	5.5	0.824263	0.8240[g]	0.82447[i]	1.4318[g]
1-decanol	99.88	5.5	0.826421	0.82698[e]	0.82623[i]	1.43549[e]

[a] Estimated by GLC analysis. [b] Determined by Karl Fischer method. [c] Ref 16. [d] Ref 17. [e] Ref 18. [f] Ref 19. [g] Ref 20. [h] Ref 21. [i] Ref 22.

Table 2. Densities (ρ) and Excess Molar Volumes (V_m^E) of (1-Alkanol + Dodecane) at 298.15 K

x	$\frac{\rho}{\mathrm{g\cdot cm^{-3}}}$	$\frac{V_m^E}{\mathrm{cm^3\cdot mol^{-1}}}$	x	$\frac{\rho}{\mathrm{g\cdot cm^{-3}}}$	$\frac{V_m^E}{\mathrm{cm^3\cdot mol^{-1}}}$	x	$\frac{\rho}{\mathrm{g\cdot cm^{-3}}}$	$\frac{V_m^E}{\mathrm{cm^3\cdot mol^{-1}}}$	x	$\frac{\rho}{\mathrm{g\cdot cm^{-3}}}$	$\frac{V_m^E}{\mathrm{cm^3\cdot mol^{-1}}}$
$x\mathrm{CH_3OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_2H_5OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_3H_7OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_4H_9OH} + (1-x)\mathrm{C_{12}H_{26}}$		
0.00135	0.745406	0.0078	0.00284	0.745404	0.0185	0.00273	0.745430	0.0173	0.00247	0.745450	0.0139
0.00185	0.745400	0.0110	0.00350	0.745397	0.0226	0.00429	0.745426	0.0269	0.00337	0.745455	0.0189
0.00406	0.745379	0.0224	0.00482	0.745386	0.0302	0.00700	0.745424	0.0422	0.00504	0.745466	0.0281
0.00925	0.745332	0.0483	0.00760	0.745363	0.0458	0.01162	0.745429	0.0659	0.00890	0.745497	0.0474
0.01113	0.745324	0.0548	0.01169	0.745338	0.0661	0.01810	0.745456	0.0931	0.01274	0.745535	0.0643
0.01828	0.745284	0.0828	0.01342	0.745329	0.0742	0.02480	0.745504	0.1152	0.01568	0.745569	0.0761
0.02969	0.745265	0.1136	0.01890	0.745313	0.0959	0.04304	0.745689	0.1601	0.02553	0.745703	0.1090
0.04640	0.745259	0.1523	0.02678	0.745305	0.1226	0.06062	0.745916	0.1901	0.04126	0.745979	0.1445
0.06420	0.745271	0.1882	0.04127	0.745348	0.1547	0.07866	0.746164	0.2180	0.06044	0.746372	0.1729
0.08321	0.745289	0.2251	0.06055	0.745432	0.1898	0.10253	0.746495	0.2572	0.07754	0.746736	0.1965
0.09518	0.745306	0.2467	0.08084	0.745514	0.2295				0.10338	0.747278	0.2391
			0.09645	0.745601	0.2535						
$x\mathrm{C_5H_{11}OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_6H_{13}OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_7H_{15}OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_8H_{17}OH} + (1-x)\mathrm{C_{12}H_{26}}$		
0.00199	0.745463	0.0108	0.00175	0.745477	0.0096	0.00183	0.745491	0.0096	0.00204	0.745513	0.0105
0.00476	0.745503	0.0250	0.00460	0.745539	0.0244	0.00384	0.745550	0.0193	0.00419	0.745594	0.0203
0.00753	0.745546	0.0380	0.00826	0.745625	0.0410	0.00719	0.745657	0.0335	0.00734	0.745718	0.0336
0.01643	0.745714	0.0721	0.01788	0.745888	0.0742	0.01509	0.745934	0.0595	0.01454	0.746026	0.0564
0.02691	0.745951	0.1010	0.02646	0.746157	0.0938	0.02602	0.746357	0.0845	0.02591	0.746560	0.0792
0.03525	0.746159	0.1186	0.03537	0.746455	0.1094	0.03537	0.746740	0.0998	0.03144	0.746830	0.0872
0.05055	0.746571	0.1433	0.04959	0.746947	0.1307	0.04943	0.747341	0.1174	0.04912	0.747720	0.1074
0.06514	0.746983	0.1632	0.06560	0.747525	0.1500	0.06486	0.748019	0.1333	0.06408	0.748489	0.1217
0.08115	0.747444	0.1846	0.07934	0.748030	0.1660	0.08181	0.748778	0.1492	0.08146	0.749394	0.1377
0.09931	0.747979	0.2082	0.09708	0.748704	0.1826	0.10235	0.749709	0.1693	0.10144	0.750468	0.1499
$x\mathrm{C_9H_{19}OH} + (1-x)\mathrm{C_{12}H_{26}}$			$x\mathrm{C_{10}H_{21}OH} + (1-x)\mathrm{C_{12}H_{26}}$								
0.00099	0.745467	0.0050	0.001264	0.745351	0.0065						
0.00470	0.745637	0.0216	0.002235	0.745401	0.0114						
0.00777	0.745786	0.0329	0.004620	0.745527	0.0223						
0.01456	0.746133	0.0527	0.011828	0.745934	0.0482						
0.02651	0.746790	0.0744	0.032299	0.747221	0.0828						
0.03533	0.747291	0.0860	0.056688	0.748861	0.0954						
0.05117	0.748212	0.1021	0.083338	0.750666	0.1093						
0.06465	0.749011	0.1131	0.106910	0.752273	0.1223						
0.08043	0.749970	0.1205									
0.09832	0.751064	0.1297									

Table 3. Coefficients (d_j) and Estimated Standard Uncertainties (u_d) Determined by Eq 7 for {x1-Alkanol + (1 − x)Dodecane} at 298.15 K

	methanol	ethanol	1-propanol	1-butanol	1-pentanol	1-hexanol	1-heptanol	1-octanol	1-nonanol	1-decanol
d_j										
d_1	0.745421	0.745440	0.745439	0.745432	0.745427	0.745440	0.745434	0.745435	0.745417	0.745285
d_2	−0.011899	−0.013325	−0.004322	0.005512	0.015009	0.019818	0.029347	0.036440	0.045763	0.050725
d_3	0.30395	0.42414	0.34415	0.22908	0.19099	0.35904	0.29561	0.35223	0.28678	0.39692
d_4	−3.2331	−4.4955	−2.9180	−1.0625	−0.8422	−3.6430	−2.6571	−3.7304	−2.7548	−3.9688
d_5	12.820	17.716	9.293			14.517	9.332	15.169	10.640	14.373
u_d/g·cm^{-3}	2.6×10^{-6}	3.0×10^{-6}	1.2×10^{-6}	3.7×10^{-6}	6.2×10^{-6}	2.4×10^{-6}	2.3×10^{-6}	2.6×10^{-6}	4.9×10^{-6}	1.2×10^{-6}

was calibrated with an estimated standard deviation of $\pm 3 \times 10^{-6}$ g·cm^{-3}.

The mixtures used to measure density were prepared in specially designed vessels of 10 cm^3 that avoid changes in x caused by evaporation into the vapor phase above the liquid.[5] The weights of sample liquids, the vapor phase, and the balance-weight were corrected against buoyancy. The uncertainty in the mole fraction for the dilute region of alkanol (δx) due to the uncertainty in weight is expressed with

$$\delta x = (M_1/M_2)(1/w_1)\ \delta w_2 \tag{1}$$

where M_1 and M_2 are the molar masses of dodecane and

Table 4. Coefficients (v_j) and Estimated Standard Uncertainty (u_v) Determined by Eq 8 for {x1-Alkanol + (1 − x)Dodecane} at 298.15 K

	methanol	ethanol	1-propanol	1-butanol	1-pentanol
v_j					
v_1	6.027	6.784	6.656	5.836	5.636
v_2	-1.0135×10^2	-96.60	-91.42	-54.03	-83.76
v_3	12.963×10^2	5.800×10^2	7.201×10^2	-3.177×10^2	7.397×10^2
v_4	-7.479×10^3	33.66×10^2	-1.903×10^3	10.380×10^3	-2.327×10^3
v_5	14.48×10^2	-3.433×10^3		-5.030×10^3	
u_v/cm^3·mol^{-1}	0.0007	0.0006	0.0007	0.0005	0.0005

	1-hexanol	1-heptanol	1-octanol	1-nonanol	1-decanol
v_j					
v_1	5.755	5.478	5.375	5.185	5.340
v_2	-1.0555×10^2	-1.2159×10^2	-1.2109×10^2	-1.3411×10^2	-1.2019×10^2
v_3	11.303×10^2	18.564×10^2	15.968×10^2	22.843×10^2	13.808×10^2
v_4	-4.453×10^3	-1.4838×10^4	-9.209×10^3	-1.9909×10^4	-7.195×10^3
v_5		48.04×10^2	16.36×10^2	67.44×10^2	13.75×10^2
u_v/cm^3·mol^{-1}	0.0007	0.0002	0.0006	0.0005	0.0009

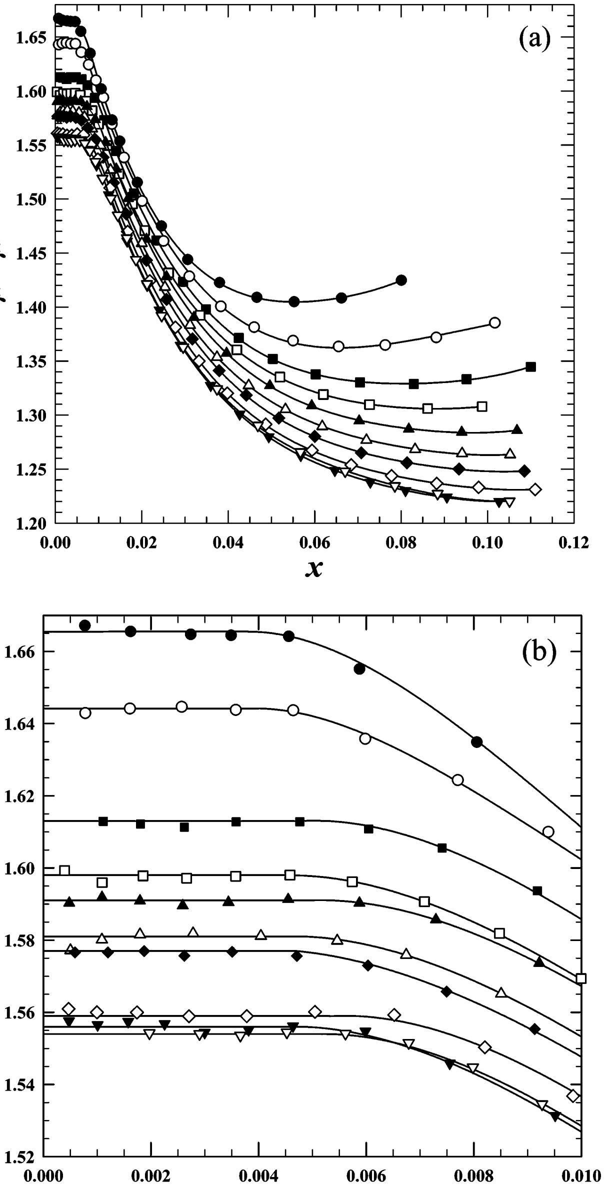

Figure 2. Observed apparent dipole moments of $C_nH_{2n+1}OH$ (μ) in dodecane at 298.15 K: ●, $n = 1$; ○, $n = 2$; ■, $n = 3$; □, $n = 4$; ▲, $n = 5$; △, $n = 6$; ◆, $n = 7$; ◇, $n = 8$; ▼, $n = 9$; ▽, $n = 10$. $\mu^* = 3.33564 \times 10^{-30}$ C·m. Lines are the least squares representation: (a) for $0 < x < 0.12$; (b) enlarged for $x < 0.01$.

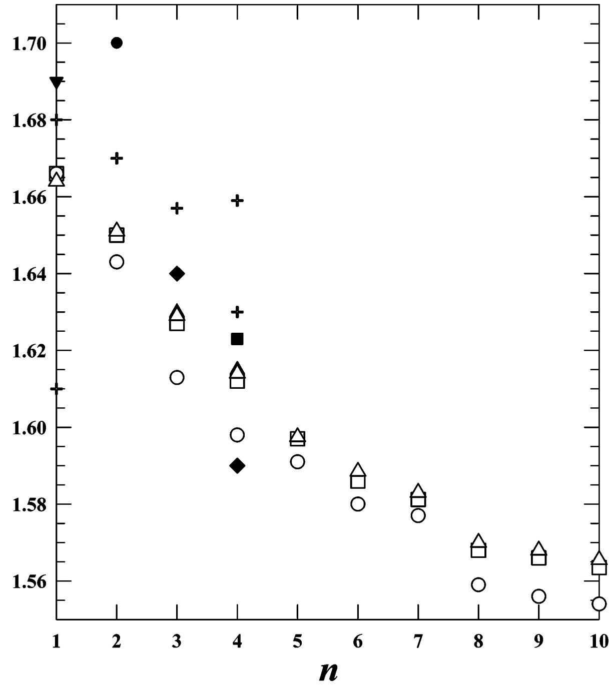

Figure 3. Dipole moments of isolated $C_nH_{2n+1}OH$ (μ_0) at 298.15 K. Our results: ○, in dodecane; △, in cyclohexane;[4] □, in heptane.[4] Literature values: +, in vapor phase;[10] ▼, in vapor phase;[11] ◆, in vapor phase;[12] ●, in cyclohexane;[9] ▲, in cyclohexane;[3] ■, in cyclohexane.[2] $\mu^* = 3.33564 \times 10^{-30}$ C·m.

1-alkanol, respectively, and w_1 and w_2 are the masses of dodecane and 1-alkanol, respectively. By adopting the estimated standard uncertainty of 0.2 mg for δw_2 the uncertainty in x reached the largest value of 1.4×10^{-4} in the case of methanol + dodecane system.

The temperature for the measurements of ρ was monitored with a thermometer (Precision Thermometry Bridge of Ninco Products, Inc., F300 MKII, England). It was calibrated with a triple-point water cell (home-made) and a Gallium cell (1740, Yellow Spring Instrument Co., USA). Thereby, the temperature was controlled at 298.15 K within an uncertainty of 0.01 K.

The excess molar volumes were calculated from density values as a function of x by the relationship:

$$V_m^E = \{(1-x)M_1 + xM_2\}/\rho - (1-x)\,M_1/\rho^*_1 - xM_2/\rho^*_2 \tag{2}$$

where ρ denotes the density of mixture; ρ^*_1 and ρ^*_2 are

Table 5. Relative Permittivities (ϵ_r) and Apparent Dipole Moments of 1-Alkanols μ(F) Calculated by Eq 4 and μ(D) by Eq 6 at 298.15 K ($\mu^* = 3.33564 \times 10^{-30}$ C·m)

x	ϵ_r	$\mu(F)/\mu^*$	$\mu(D)/\mu^*$	x	ϵ_r	$\mu(F)/\mu^*$	$\mu(D)/\mu^*$	x	ϵ_r	$\mu(F)/\mu^*$	$\mu(D)/\mu^*$	x	ϵ_r	$\mu(F)/\mu^*$	$\mu(D)/\mu^*$
xCH$_3$OH + $(1 - x)$C$_{12}$H$_{26}$				xC$_2$H$_5$OH + $(1 - x)$C$_{12}$H$_{26}$				xC$_3$H$_7$OH + $(1 - x)$C$_{12}$H$_{26}$				xC$_4$H$_9$OH + $(1 - x)$C$_{12}$H$_{26}$			
0.000771	2.008222	1.667	1.648	0.000779	2.008124	1.643	1.639	0.001113	2.008412	1.613	1.619	0.000394	2.007748	1.599	1.612
0.001621	2.009272	1.666	1.646	0.001608	2.009152	1.644	1.640	0.001805	2.009261	1.612	1.619	0.001092	2.008608	1.596	1.608
0.002740	2.010659	1.665	1.646	0.002571	2.010350	1.645	1.640	0.002620	2.010262	1.611	1.618	0.001852	2.009553	1.598	1.610
0.003489	2.011589	1.664	1.645	0.003578	2.011599	1.644	1.639	0.003582	2.011456	1.613	1.619	0.002663	2.010557	1.597	1.609
0.004562	2.012925	1.664	1.645	0.004642	2.012927	1.644	1.639	0.004766	2.012923	1.613	1.619	0.003575	2.011694	1.598	1.610
0.005874	2.014482	1.655	1.636	0.005982	2.014531	1.636	1.631	0.006045	2.014492	1.611	1.617	0.004582	2.012951	1.598	1.610
0.008056	2.016939	1.635	1.615	0.007701	2.016532	1.624	1.620	0.007410	2.016128	1.606	1.611	0.005742	2.014384	1.596	1.608
0.010608	2.019513	1.602	1.583	0.009387	2.018400	1.610	1.605	0.009180	2.018154	1.594	1.599	0.007082	2.015999	1.591	1.602
0.013096	2.021872	1.573	1.554	0.011113	2.020222	1.594	1.589	0.011305	2.020401	1.573	1.578	0.008478	2.017621	1.582	1.593
0.014907	2.023498	1.554	1.535	0.013085	2.022090	1.569	1.564	0.014079	2.023126	1.545	1.550	0.009996	2.019302	1.569	1.581
0.018967	2.026970	1.515	1.497	0.015887	2.024614	1.538	1.533	0.018183	2.016847	1.505	1.510	0.011960	2.021339	1.550	1.561
0.02456	2.031548	1.475	1.457	0.02008	2.028153	1.498	1.493	0.02340	2.031194	1.462	1.466	0.014717	2.024049	1.523	1.534
0.03063	2.036439	1.444	1.425	0.02502	2.032142	1.461	1.456	0.02953	2.036123	1.423	1.427	0.01783	2.026932	1.495	1.506
0.03798	2.042625	1.423	1.404	0.03098	2.036888	1.428	1.423	0.03486	2.040329	1.398	1.401	0.02067	2.029389	1.471	1.481
0.04663	2.050229	1.409	1.390	0.03829	2.042741	1.401	1.395	0.04243	2.046346	1.371	1.374	0.02620	2.033992	1.432	1.441
0.05524	2.058340	1.405	1.385	0.04601	2.049071	1.381	1.375	0.05033	2.052715	1.352	1.355	0.03349	2.039841	1.392	1.401
0.06621	2.069539	1.408	1.388	0.05500	2.056819	1.369	1.362	0.06022	2.061082	1.338	1.340	0.04201	2.046631	1.360	1.368
0.08007	2.085608	1.425	1.403	0.06553	2.066488	1.363	1.356	0.07048	2.070192	1.330	1.332	0.05197	2.054660	1.335	1.343
				0.07632	2.077165	1.365	1.357	0.08292	2.082062	1.329	1.329	0.06201	2.062984	1.319	1.326
				0.08814	2.089857	1.372	1.363	0.09516	2.094737	1.333	1.333	0.07269	2.072278	1.310	1.316
				0.10170	2.105961	1.385	1.375	0.10999	2.111571	1.345	1.343	0.08613	2.084755	1.306	1.311
												0.09876	2.097321	1.308	1.313
xC$_5$H$_{11}$OH + $(1 - x)$C$_{12}$H$_{26}$				xC$_6$H$_{13}$OH + $(1 - x)$C$_{12}$H$_{26}$				xC$_7$H$_{15}$OH + $(1 - x)$C$_{12}$H$_{26}$				xC$_8$H$_{17}$OH + $(1 - x)$C$_{12}$H$_{26}$			
0.000482	2.007671	1.590	1.607	0.000504	2.007990	1.577	1.598	0.000586	2.007864	1.577	1.600	0.000468	2.007818	1.561	1.586
0.001089	2.008436	1.592	1.609	0.001087	2.008731	1.580	1.600	0.001199	2.008654	1.577	1.600	0.000994	2.008496	1.560	1.585
0.001796	2.009324	1.591	1.608	0.001795	2.009633	1.582	1.602	0.001873	2.009525	1.577	1.600	0.001740	2.009458	1.560	1.585
0.002589	2.010318	1.590	1.606	0.002783	2.010894	1.582	1.602	0.002621	2.010487	1.576	1.598	0.002707	2.010704	1.559	1.584
0.003440	2.011396	1.591	1.607	0.004043	2.012498	1.581	1.601	0.003507	2.011638	1.577	1.599	0.003781	2.012094	1.559	1.584
0.004549	2.012804	1.591	1.608	0.005459	2.014299	1.580	1.600	0.004712	2.013193	1.576	1.598	0.005049	2.013748	1.560	1.585
0.005875	2.014478	1.590	1.607	0.006744	2.015904	1.576	1.596	0.006033	2.014886	1.573	1.595	0.006519	2.015655	1.559	1.584
0.007295	2.016230	1.586	1.602	0.008507	2.018017	1.565	1.585	0.007493	2.016697	1.566	1.588	0.008207	2.017743	1.550	1.575
0.009216	2.018495	1.574	1.589	0.010459	2.020240	1.550	1.569	0.009131	2.018667	1.555	1.577	0.009844	2.019660	1.537	1.561
0.011622	2.021135	1.552	1.568	0.012777	2.022690	1.527	1.545	0.011034	2.020819	1.539	1.560	0.012661	2.022753	1.510	1.534
0.014101	2.023652	1.528	1.543	0.016562	2.026391	1.490	1.508	0.013453	2.023382	1.515	1.536	0.016705	2.026791	1.470	1.493
0.01688	2.026285	1.501	1.515	0.02000	2.029519	1.459	1.476	0.01639	2.026282	1.486	1.507	0.02183	2.031464	1.424	1.446
0.02110	2.030031	1.463	1.477	0.02535	2.034118	1.419	1.435	0.02108	2.030551	1.443	1.463	0.02777	2.036520	1.381	1.402
0.02571	2.033879	1.428	1.442	0.03116	2.038875	1.383	1.399	0.02571	2.034487	1.407	1.426	0.03323	2.041006	1.350	1.370
0.03208	2.039026	1.391	1.403	0.03741	2.043878	1.354	1.369	0.03171	2.039427	1.371	1.389	0.03980	2.046276	1.320	1.340
0.03962	2.044995	1.357	1.369	0.04472	2.049696	1.327	1.342	0.03790	2.044405	1.341	1.359	0.04865	2.053382	1.292	1.310
0.04963	2.052978	1.327	1.339	0.05324	2.056521	1.305	1.319	0.04415	2.049401	1.318	1.335	0.05937	2.062047	1.267	1.285
0.05931	2.060899	1.309	1.319	0.06176	2.063462	1.290	1.303	0.05170	2.055433	1.297	1.314	0.06843	2.069532	1.254	1.271
0.07029	2.070108	1.295	1.305	0.07197	2.072000	1.277	1.290	0.06004	2.062194	1.280	1.296	0.07780	2.077407	1.244	1.260
0.08177	2.080230	1.287	1.296	0.08324	2.081771	1.268	1.281	0.07079	2.071112	1.265	1.280	0.08823	2.086476	1.237	1.253
0.09402	2.091619	1.284	1.293	0.09410	2.091640	1.264	1.276	0.08135	2.080160	1.256	1.270	0.09795	2.095204	1.233	1.248
0.10681	2.104290	1.286	1.294	0.10523	2.102215	1.263	1.274	0.09339	2.090889	1.250	1.264	0.11105	2.107428	1.231	1.246
								0.10854	2.105048	1.248	1.261				
xC$_9$H$_{19}$OH + $(1 - x)$C$_{12}$H$_{26}$								xC$_{10}$H$_{21}$OH + $(1 - x)$C$_{12}$H$_{26}$							
0.000477	2.007822	1.558	1.585	0.02124	2.031180	1.420	1.443	0.001971	2.009738	1.554	1.583	0.01864	2.029002	1.444	1.470
0.001008	2.008517	1.557	1.584	0.02410	2.033697	1.397	1.420	0.002902	2.010975	1.554	1.583	0.02121	2.031366	1.421	1.447
0.001576	2.009265	1.557	1.585	0.02897	2.037840	1.364	1.387	0.003662	2.011985	1.554	1.582	0.02459	2.034256	1.392	1.417
0.002254	2.010153	1.557	1.584	0.03592	2.043555	1.327	1.349	0.004525	2.013140	1.554	1.583	0.02958	2.038642	1.363	1.387
0.002998	2.011122	1.554	1.581	0.04265	2.049022	1.301	1.321	0.005614	2.014591	1.554	1.583	0.03739	2.045142	1.324	1.348
0.003815	2.012200	1.555	1.582	0.04937	2.054450	1.280	1.300	0.006788	2.016132	1.552	1.580	0.04685	2.052861	1.290	1.313
0.004639	2.013292	1.556	1.583	0.05678	2.060471	1.263	1.282	0.007983	2.017642	1.545	1.573	0.05669	2.060885	1.266	1.288
0.005985	2.015058	1.555	1.581	0.06467	2.066955	1.249	1.267	0.009268	2.019198	1.535	1.563	0.06704	2.069450	1.248	1.269
0.007553	2.017027	1.546	1.572	0.07288	2.073812	1.238	1.256	0.010893	2.021070	1.519	1.547	0.07856	2.079149	1.234	1.255
0.009513	2.019390	1.531	1.557	0.08103	2.080753	1.230	1.248	0.012832	2.023212	1.501	1.528	0.08846	2.087731	1.227	1.247
0.012351	2.022553	1.504	1.529	0.09058	2.089102	1.224	1.241	0.014453	2.024922	1.485	1.512	0.10509	2.102617	1.220	1.239
0.01662	2.026872	1.461	1.485	0.10266	2.099992	1.220	1.237	0.01654	2.027001	1.464	1.490				

the densities of dodecane and 1-alkanol in pure state, respectively; and M_1 and M_2 are the molar masses of dodecane and 1-alkanol, respectively. The uncertainty in excess volume (δV_m^E) was propagated from the uncertainty in the mole fraction (δx) and that in the density of mixture ($\delta\rho$). It was expressed for a region of $x < 0.1$ by

$$\delta V_m^E = M_2(1/\rho^*_1 - 1/\rho^*_2)\,\delta x + (1/\rho^2)\{xM_2 + (1 - x)M_1\}\,\delta\rho \quad (3)$$

The uncertainty in the densities of pure liquid was negligible because relative values in density between the mixture and the component liquid determine the excess volumes. The deviation of V_m^E propagated from the density of mixture ($\delta\rho$) was about 9×10^{-4} cm^3·mol^{-1} and that propagated from δx was (3 to 6) $\times 10^{-4}$ cm^3·mol^{-1}. Accordingly, the combined standard uncertainty in V_m^E was estimated to be (9.5 to 10.9) $\times 10^{-4}$ cm^3·mol^{-1}.

The relative permittivities (ϵ_r) were measured with a LCR meter (HP-4284A). A stepwise dilution method was

Table 6. Dipole Moments (μ_0) of $C_nH_{2n+1}OH$ at Infinite Dilution for $T = 298.15$ K Calculated by Eq 4 ($\mu^* = 3.33564 \times 10^{-30}$ C·m)

	μ_0/μ^*							
	in dodecane	in heptane	in cyclohexane			in vapor		
n	present work	previous work[a]	previous work[a]	lit.	lit.	lit.	lit.	lit.
1	1.666	1.666	1.664			1.69[f]	1.61[e]	1.68[e]
2	1.644	1.650	1.652	1.700[b]		1.67[e]		
3	1.613	1.627	1.629	1.630[c]		1.64[g]	1.657[e]	
4	1.598	1.612	1.614	1.623[d]	1.615[c]	1.63[e]	1.659[e]	1.59[g]
5	1.591	1.597	1.598					
6	1.581	1.586	1.589					
7	1.577	1.581	1.583					
8	1.559	1.568	1.570					
9	1.556	1.566	1.568					
10	1.554	1.564	1.566					

[a] Previous results reported in ref 4. [b] Ref 9. [c] Ref 3. [d] Determined graphically from ref 2. [e] Ref 10. [f] Ref 11. [g] Ref 12.

applied for fillings of the electrode cell with solution. The electrode cell, which consists of two cylindrical nickel plates, had a capacitance (C) of 28 pF. The value of C was measured with an repeatability of ± 0.0001 pF, which corresponded to an uncertainty of $\pm\ 3.5 \times 10^{-6}$ in ϵ_r. The Frohlich equation,[6]

$$V_m(\epsilon_r - 1)/3\epsilon_r = (1 - x)V^*_1(\epsilon^*_{r,1} - 1)/(\epsilon^*_{r,1} + 2\epsilon_r) + xV^*_2(\epsilon_{r,2}' - 1)/(\epsilon_{r,2}' + 2\epsilon_r) + 4\pi N_A x g \mu_0^2(\epsilon_{r,2}' + 2)^2(2\epsilon_r + 1)/27kT(\epsilon_{r,2}' + 2\epsilon_r)^2 \quad (4)$$

was used to calculate μ values. It is expressed in terms of relative permittivity for the solution, ϵ_r, that for dodecane, $\epsilon^*_{r,1}$, the molar volume of the solution, V_m, the molar volume of dodecane, V^*_1, the molar volume of 1-alkanol, V^*_2, and the "internal permittivity" of 1-alkanol, $\epsilon_{r,2}'$ activated by infrared radiation. Here, N_A is Avogadro constant, k is Boltzmann constant, and g is the "Kirkwood g-factor".[7] The apparent dipole moment (μ) is defined as $\mu = (g\mu^2_0)^{1/2}$. We calculated $\epsilon_{r,2}'$ from the Clausius−Mossotti equation, adopting the atomic polarization (P_A) that was evaluated using the assumed relation:

$$P_E + P_A = 1.10P_E \quad (5)$$

where P_E was calculated by the Lorenz−Lorentz equation using the refractive index for the sodium-D line, n_D. We also calculated μ values by Debye equation:

$$V_m(\epsilon_r - 1)/(\epsilon_r + 2) = (1 - x)V^*_1(\epsilon^*_{r,1} - 1)/(\epsilon^*_{r,1} + 2) + xV^*_2(\epsilon_r - 1)/(\epsilon_r + 2) + 4\pi N_A x \mu_0^2/9kT \quad (6)$$

We used the same equations for eqs 4 to 6 as those used by French et al.[2] so that the experimental results can be compared based on the same method of calculation.

The expanded uncertainty in μ_0 (with a coverage factor, $k = 2$) was estimated to be 0.002 D by means of simulations adopting the uncertainty in ϵ_r to eq 4, where D = 3.33564×10^{-30} C·m. The experimental techniques for V^E_m and μ measurements have been described in detail in the previous reports.[3,4]

Results and Discussion

Excess Volume. The values of ρ and V^E_m are listed in Table 2. The function

$$\rho/(\mathrm{g{\cdot}cm^{-3}}) = \sum d_j x^{(j-1)} \quad (7)$$

was fitted to each set of densities, and the smoothing function

$$V^E_m/(\mathrm{cm^3{\cdot}mol^{-1}}) = x(1 - x)\sum v_j x^{(j-1)} \quad (8)$$

was fitted to excess volumes by the least-squares method. The values of coefficients (d_j) and the estimated standard uncertainties (u_d) determined for eq 7 are summarized in Table 3. The coefficients of v_i are listed in Table 4 with the estimated standard uncertainty, u_v. In Figure 1, the excess partial molar volumes of 1-alkanol at the infinite dilution ($V_2^{E,\infty}$), the numerical value of which equals to v_1 of eq 8, are plotted along with our previous results for 1-alkanols determined in cyclohexane and heptane and also with literature values measured in alkanes at 298.15 K. The limiting value ($V_2^{E,\infty}$) is defined by

$$V_2^{E,\infty} = V_2^{\infty} - V_2^* \quad (9)$$

where V_2^{∞} and V_2^* are the partial molar volumes of alkanol at infinite dilution and in pure state, respectively. Therefore, $V_2^{E,\infty}$ denotes the change in partial molar volume of alkanol performed by the transfer between the two media of pure alkanol and an alkane. The uncertainty at the vicinity of the infinite dilution varied depending on the system, and it was estimated to be less than ± 0.9 cm³·mol⁻¹. For all the alkanols the values of $V_2^{E,\infty}$ in cyclohexane were the same within the experimental uncertainty. On the other hand, $V_2^{E,\infty}$ in n-alkane decreased systematically with increasing chain length of 1-alkanol. The value of methanol was constant, irrespective of solvent, and it was $(7.6 \pm 0.7)\ \mathrm{cm^3{\cdot}mol^{-1}}$.

Apparent Dipole Moment. To investigate the dielectric relaxation we measured the relative permittivities for 1-butanol + cyclohexane at frequencies of 20, 30, and 100 kHz. The calculated values of μ at these frequencies agreed within 0.001 D over the observed mole fraction. Therefore, we concluded that the dielectric loss is negligible at the frequency lower than 100 kHz. We employed the capacitances measured at the frequency of 30 kHz because the C value fluctuated due to the metal stirrer placed in the oil bath at a frequency lower than 20 kHz. The experimental results for ϵ_r and μ calculated by the Frohlich and Debye equations are listed in Table 5. Frohlich equation gave a larger value for μ_0 of methanol and ethanol than that calculated by Debye equation, whereas Debye equation gave larger values as the chain length of alkanol increased. A maximum difference, viz., 0.03 D, occurred for 1-decanol. The Frohlich equation is based on the cavity field and the reaction field proposed by Onsager.[8] The difference found in the calculated μ values resulted from these two equations were discussed from a viewpoint of the reaction field in the previous publications.[4,9]

The μ values determined by Frohlich equation are represented in Figure 2, where the curves are least squares representations. An enlarged plots for a region of $x < 0.01$ is shown in Figure 2b. The value of μ was constant in the region of $x < 0.006$ for each alkanol and decreased sharply due to the onset of intermolecular association of alkanols. These aspects have been commonly observed in binary systems consist of alkanol and nonpolar solvent.[2−4,9] The dipole moments of isolated alkanols (μ_0) were determined by taking an average for the points that had a constant value independent of x.

The present results for μ_0 calculated by Frohlich equation are listed in Table 6 with literature values. Here the values measured in vapor phase were calculated by the Debye equation, and our previous results determined in cyclohexane and heptane were determined by the Frohlich equation. Those values of μ_0 are plotted in Figure 3.

The observed values of μ_0 for methanol were the same within ± 0.001 D, irrespective of the three tested solvents, whereas it decreased with increasing chain-length of 1-alkanol. Small but systematic changes in μ_0 due to solvent were observed for each alkanol except for methanol. The magnitude of μ_0 of each alkanol was largest in cyclohexane and decreased in straight-chain hydrocarbons. The value in dodecane was smaller than that in heptane exceeding the uncertainty of determination. We found that the dipole moment of 1-alkanol varies with the relative direction of the group moment of -OH and the terminal group of -CH_3 by means of ab initio calculations.[4] The present experimental results imply that the rotation of the segments in alkanol is restricted in a solvent of straight and long-chain hydrocarbon due to the dispersion force that acts between the hydrocarbons of solute and solvent molecules. A restricted rotation of the segments of alkanols in a long-chain alkane would reveal this behavior.

Marsh and co-workers determined the dipole moments of 1-alkanols in various solvents at different temperatures by means of the Frohlich equation.[2,9] Our values for 1-butanol in cyclohexane agreed with their value with a difference less than 0.01 D. The determinations in vapor phase have been carried out based on the Debye equation assuming independence of temperature over a range of 100 K. The values in vapor phase reported by Wesson,[10] Ramswamy,[11] and Kubo[12] showed considerable discrepancies. We did not find the values of 1-alkanols for $n \geq 5$ measured in vapor phase.

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