Excess Molar Volumes and Refractive Indices of *cis*-9-Octadecenoic Acid + *n*-Alkanes or Alkan-1-ols at 298.15 K

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The excess molar volumes V_m^E and refractive indices n_D of *cis*-9-octadecenoic (oleic) acid + a *n*-alkane (C_7–C_{12}) or + an alkan-1-ol (C_6–C_{12}) have been determined at 298.15 K for all mixtures. The excess volumes are negative over the whole composition range. A linear dependence between V_m^E at the minimum and the number of carbon atoms, N_C, and between $V_m^E(x=0.5)$ and the volume fraction, ϕ_1, of the second component is found. Molar refractions have been derived from refractive indices and densities using the Lorenz–Lorentz equation.

Introduction

cis-9-Octadecenoic acid ($C_8H_{17}CH{=}CHC_7H_{14}CO_2H$) (oleic acid) is one of the main constituents of various vegetable oils and lipids making up biological membranes and is of considerable importance in the soap and food industries (*1*).

In previous papers (*2, 3*) we have studied H_m^E and V_m^E and binary mixtures of oleic acid + benzene, cyclohexane, hexane, trichloroethene, or tetrachloroethene at 298.15 K. In the present study values of V_m^E and n_D for x oleic acid + $(1-x)$ *n*-alkanes (heptane, octane, nonane, decane, and dodecane) or alkan-1-ols (hexan-1-ol, heptan-1-ol, octan-1-ol, nonan-1-ol, decan-1-ol, and dodecan-1-ol) are reported. The binary mixture of oleic acid with *n*-alkane is known as a system of associated and nonassociating molecules, while in the case of alkan-1-ols they not only contain self-associated species, but also show cross association between oleic acid and alkan-1-ol. The result will be used to analyze effects of the aliphatic chain length and –OH group on the measured properties.

Experimental Section

cis-9-Octadecenoic acid (BDH) was checked for purity by GLC (92% oleic acid, 4.5% linoleic acid, 2.1% stearic acid, and 1.4% palmitic acid) and was stored frozen under nitrogen atmosphere in order to avoid oxidation by air. All the remaining chemicals were products from Fluka, and their purity was better than 99% as determined by GLC. They were carefully dried with an activated molecular sieve prior to making up mixtures by weight.

The densities, ρ, of the pure components and their binary mixtures were made with an Anton Paar vibrating-tube densimeter, and the corresponding refractive indices, n_D, were measured with an Abbe refractometer (Atago 308). The details of measurements, ρ and n_D, are described elsewhere (*2, 4*). The temperature in the densimeter and refractometer was regulated through a cascade water bath apparatus (Heto) with a stability within ±0.01 K as checked by a digital precision thermometer (Anton Paar DT 100–20). Density values and refractive index values have an uncertainty of $\pm 8 \times 10^{-6}$ g cm^{-3} and $\pm 10^{-4}$, respectively.

For the pure compounds, the densities measured at 298.15 K were 0.679 25 g cm^{-3}, heptane; 0.698 29 g cm^{-3}, octane; 0.713 85 g cm^{-3}, nonane; 0.726 20 g cm^{-3}, decane; 0.745 67 g cm^{-3}, dodecane; 0.815 01 g cm^{-3}, hexan-1-ol; 0.818 91 g cm^{-3}, heptan-1-ol; 0.821 48 g cm^{-3}, octan-1-ol; 0.824 28 g cm^{-3}, nonan-1-ol; 0.826 15 g cm^{-3}, decan-1-ol; and 0.829 73 g cm^{-3}, dodecan-1-ol. These values are in reasonable agreement with those compiled by the literature. The precision of the excess molar volume is within ±0.002 cm^3 mol^{-1}.

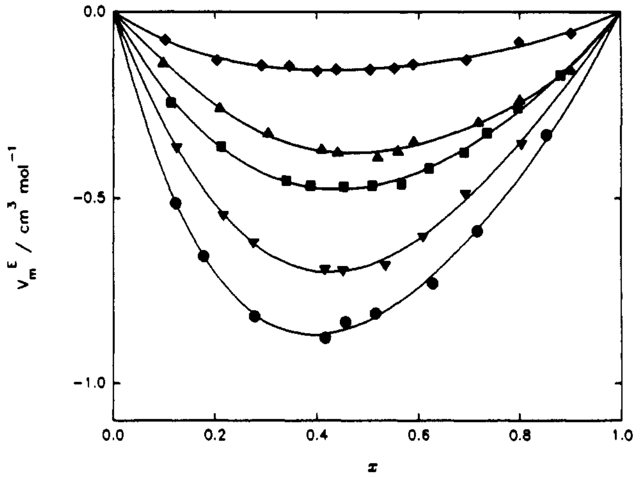

Figure 1. Excess molar volumes V_m^E of x oleic acid + $(1-x)$ *n*-alkane at 298.15 K: heptane; ▼, octane; ■, nonane; ▲, decane; ♦, dodecane; —, calculated from eq 1 with the coefficients from Table III.

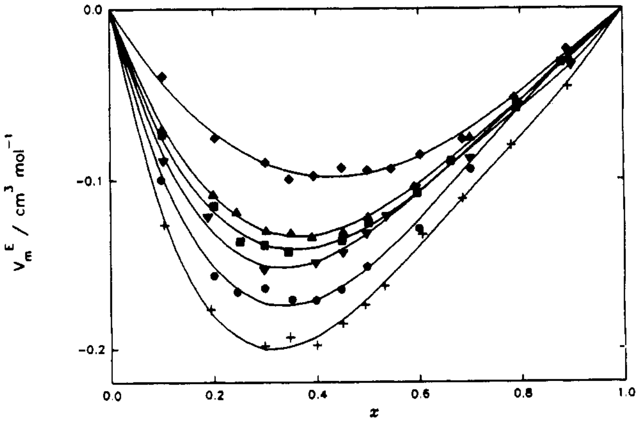

Figure 2. Excess molar volumes V_m^E of x oleic acid + $(1-x)$ alkan-1-ol at 298.15 K: +, hexan-1-ol; ●, heptan-1-ol; ▼, octan-1-ol; ■, nonan-1-ol; ▲, decan-1-ol; ♦, dodecan-1-ol; —, calculated from eq 1 with the coefficients from Table III.

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Table I. Densities ρ, Excess Molar Volumes V_m^E, Refractive Indices n_D, and Molar Refractions $[R]_{12}$ for x *cis*-$C_8H_{17}CH{=}CHC_7H_{14}CO_2H$ + $(1 - x)$ C_7H_{16}, C_8H_{18}, C_9H_{20}, $C_{10}H_{22}$, or $C_{12}H_{26}$ at 298.15 K

x	ρ/ (g cm^{-3})	V_m^E/ (cm^3 mol^{-1})	n_D	$[R]_{12}$	x	ρ/ (g cm^{-3})	V_m^E/ (cm^3 mol^{-1})	n_D	$[R]_{12}$
C_7H_{16}									
0.0	0.679 25		1.3856	34.62	0.5144	0.828 20	−0.812	1.4386	61.55
0.1224	0.730 01	−0.514	1.4043	41.07	0.6273	0.846 38	−0.731	1.4450	67.46
0.1777	0.748 74	−0.657	1.4110	43.97	0.7156	0.858 53	−0.590	1.4480	71.92
0.2783	0.776 69	−0.821	1.4212	49.30	0.8531	0.874 82	−0.329	1.4544	79.29
0.4163	0.809 77	−0.878	1.4324	56.45	1.0	0.889 40		1.4590	86.82
0.4560	0.817 50	−0.836	1.4350	58.51					
C_8H_{16}									
0.0	0.698 29		1.3958	39.29	0.5334	0.832 35	−0.682	1.4404	64.63
0.1242	0.741 02	−0.363	1.4102	45.20	0.6067	0.843 55	−0.605	1.4444	68.21
0.2160	0.767 02	−0.547	1.4190	49.57	0.6925	0.855 37	−0.488	1.4480	72.21
0.2757	0.781 86	−0.621	1.4238	52.40	0.8032	0.869 05	−0.353	1.4528	77.53
0.4152	0.811 52	−0.693	1.4334	59.00	1.0	0.889 40		1.4590	86.82
0.4507	0.818 14	−0.696	1.4358	60.71					
C_9H_{20}									
0.0	0.713 85		1.4042	43.96	0.5650	0.837 64	−0.462	1.4436	68.25
0.1133	0.747 13	−0.243	1.4154	48.89	0.6202	0.845 57	−0.420	1.4452	70.50
0.2121	0.771 78	−0.361	1.4232	53.13	0.6901	0.855 01	−0.377	1.4480	73.48
0.3399	0.799 09	−0.453	1.4316	58.60	0.7352	0.860 68	−0.324	1.4502	75.48
0.3875	0.808 14	−0.466	1.4342	60.61	0.7955	0.867 88	−0.256	1.4524	78.06
0.4527	0.819 69	−0.469	1.4382	63.46	0.8806	0.877 56	−0.229	1.4558	81.76
0.5080	0.828 81	−0.466	1.4400	65.70	1.0	0.889 40		1.4590	86.82
$C_{10}H_{22}$									
0.0	0.726 20		1.4098	48.53	0.5588	0.837 12	−0.373	1.4431	69.88
0.0985	0.751 25	−0.136	1.4186	52.43	0.5902	0.841 55	−0.348	1.4447	71.12
0.2095	0.776 14	−0.257	1.4250	56.55	0.7177	0.858 43	−0.295	1.4496	75.98
0.3048	0.795 11	−0.325	1.4307	60.20	0.7992	0.868 19	−0.235	1.4526	79.12
0.4098	0.813 83	−0.368	1.4364	64.22	0.9009	0.879 48	−0.156	1.4558	82.98
0.4413	0.819 07	−0.377	1.4382	65.46	1.0	0.889 40		1.4590	86.82
0.5187	0.831 24	−0.390	1.4414	68.36					
$C_{12}H_{26}$									
0.0	0.745 67		1.4197	57.77	0.5037	0.830 25	−0.154	1.4431	72.44
0.1022	0.765 55	−0.075	1.4253	60.76	0.5513	0.836 78	−0.151	1.4450	73.84
0.2038	0.783 81	−0.129	1.4305	63.74	0.5887	0.841 75	−0.140	1.4461	74.89
0.2923	0.798 55	−0.143	1.4344	66.29	0.6942	0.855 20	−0.128	1.4499	77.97
0.3468	0.807 16	−0.144	1.4368	67.88	0.7980	0.867 50	−0.081	1.4531	80.97
0.4013	0.815 49	−0.157	1.4391	69.47	0.9019	0.879 13	−0.057	1.4562	83.97
0.4390	0.821 03	−0.154	1.4405	70.55	1.0	0.889 40		1.4590	86.82

Results and Discussion

Tables I and II report the V_m^E and n_D results at 298.15 K. They were smoothed by an unweighted least-squares method to the equation

$$V_m^E = x(1-x)\sum_{i=1}^{n} A_i(1-2x)^{i-1} \tag{1}$$

where x is the mole fraction of oleic acid and V_m^E is the excess volume. The coefficients A_i and standard deviations $s(V_m^E)$ are summarized in Table III. Graphical representations of the above equation are shown in Figures 1 and 2, where the continuous lines are calculated values. The excess molar volumes, V_m^E, of oleic acid + *n*-alkane or + alkan-1-ol are negative over the whole composition range and decrease with the increase in the aliphatic chain length of the second component for both series. The inclusion of a –OH group in the *n*-alkane molecule leads to more positive V_m^E values. The observed minima shift slightly to higher mole fractions of oleic acid for all mixtures, this effect being more marked in the case of alkan-1-ols. It is interesting to note that in binary mixtures of *n*-alkanes with alkanols (*5*), excess molar volumes exhibit more negative values with increasing chain length of the alkanol. An opposite effect of that was observed by us.

In the liquid state, fatty acids, like oleic acid, form cyclic dimers through hydrogen bonds (*6*), where their molecules are orientationally correlated in parallel disposition.

The negative contribution to V_m^E observed with *n*-alkanes is principally due to the geometrical fitting in the ordered oleic acid structure. This fact is favored with a decrease of the aliphatic chain length of the *n*-alkane, whereas in the case of alkan-1-ols there is a second factor that contributes positively to V_m^E, i.e., the disruption of the hydrogen-bonded alkanol structure by the presence of oleic acid (*7*). Both oleic acid + *n*-alkane mixtures and oleic acid + alkan-1-ol mixtures show a linear dependence between excess molar volumes at the minimum, V^E_{min}, and the number of carbon atoms, N_C, or between $V_m^E(x{=}0.5)$ and the volume fraction of the second component, ϕ_1. The following expressions for the above mixtures were obtained:

n-alkanes

$$V^E_{min} = 0.143N_C - 1.832; \quad s = 0.022 \tag{2}$$

$$V^E_m(x{=}0.5) = 6.769\phi_1 - 2.963; \quad s = 0.012 \tag{3}$$

alkan-1-ols

$$V^E_{min} = 0.016N_C - 0.283; \quad s = 0.0018 \tag{4}$$

$$V^E_m(x{=}0.5) = 0.539\phi_1 - 0.320; \quad s = 0.00004 \tag{5}$$

where s denotes standard deviations.

Table II. Densities ρ, Excess Molar Volumes V_m^E, Refractive Indices n_D, and Molar Refractions $[R]_{12}$ for x *cis*-$C_8H_{17}CH{=}CHC_7H_{14}CO_2H$ + $(1 - x)$ $C_6H_{14}O$, $C_7H_{16}O$, $C_8H_{18}O$, $C_9H_{20}O$, $C_{10}H_{22}O$, or $C_{12}H_{26}O$ at 298.15 K

x	ρ/(g cm^{-3})	V_m^E/(cm^3 mol^{-1})	n_D	$[R]_{12}$	x	ρ/(g cm^{-3})	V_m^E/(cm^3 mol^{-1})	n_D	$[R]_{12}$
$C_6H_{14}O$									
0.0	0.815 01		1.4161	31.47	0.4941	0.868 68	−0.174	1.4470	58.83
0.1039	0.832 65	−0.126	1.4262	37.22	0.5326	0.870 89	−0.163	1.4485	60.98
0.1937	0.844 09	−0.176	1.4327	42.19	0.6059	0.874 69	−0.132	1.4506	65.03
0.2986	0.854 55	−0.198	1.4388	48.00	0.6855	0.878 38	−0.111	1.4527	69.43
0.3478	0.858 63	−0.193	1.4413	50.74	0.7809	0.882 24	−0.080	1.4550	74.72
0.3999	0.862 58	−0.198	1.4435	53.62	0.8924	0.886 16	−0.045	1.4571	80.87
0.4505	0.865 99	−0.185	1.4455	56.42	1.0	0.889 40		1.4590	86.82
$C_7H_{16}O$									
0.0	0.818 91		1.4224	36.09	0.4478	0.865 00	−0.165	1.4465	58.83
0.0987	0.833 30	−0.100	1.4299	41.10	0.4984	0.868 10	−0.151	1.4481	61.40
0.2001	0.844 95	−0.156	1.4360	46.25	0.5995	0.873 65	−0.129	1.4510	66.53
0.2458	0.849 40	−0.166	1.4385	48.60	0.7023	0.878 49	−0.094	1.4535	71.74
0.2996	0.854 10	−0.164	1.4409	51.32	0.7928	0.882 20	−0.055	1.4553	76.32
0.3523	0.858 32	−0.170	1.4430	53.98	0.8941	0.885 93	−0.025	1.4572	81.45
0.3984	0.861 69	−0.171	1.4448	56.33	1.0	0.889 40		1.4590	86.82
$C_8H_{18}O$									
0.0	0.821 48		1.4277	40.76	0.5362	0.869 37	−0.122	1.4500	65.49
0.1031	0.834 67	−0.089	1.4336	45.49	0.5944	0.872 52	−0.105	1.4515	68.18
0.1884	0.843 63	−0.122	1.4380	49.45	0.7007	0.877 70	−0.068	1.4538	73.07
0.2983	0.853 39	−0.153	1.4426	54.52	0.7939	0.881 79	−0.056	1.4556	77.35
0.3986	0.860 83	−0.149	1.4460	59.14	0.8993	0.885 91	−0.033	1.4575	82.20
0.4516	0.864 33	−0.143	1.4477	61.59	1.0	0.889 40		1.4590	86.82
0.4972	0.867 12	−0.132	1.4490	63.70					
$C_9H_{20}O$									
0.0	0.824 28		1.4319	45.38	0.4498	0.863 67	−0.136	1.4484	64.03
0.1008	0.835 60	−0.073	1.4366	49.56	0.5009	0.866 76	−0.126	1.4496	66.14
0.1999	0.845 07	−0.115	1.4406	53.67	0.5962	0.872 06	−0.108	1.4518	70.09
0.2516	0.849 50	−0.136	1.4424	55.81	0.6634	0.875 46	−0.089	1.4532	72.87
0.2993	0.853 25	−0.138	1.4441	57.80	0.7913	0.881 31	−0.058	1.4555	78.15
0.3459	0.856 71	−0.142	1.4455	59.73	0.8791	0.884 90	−0.031	1.4570	81.79
0.3959	0.860 17	−0.140	1.4470	61.81	1.0	0.889 40		1.4590	86.82
$C_{10}H_{22}O$									
0.0	0.826 15		1.4355	50.05	0.4515	0.863 10	−0.131	1.4492	66.64
0.1012	0.836 38	−0.070	1.4392	53.75	0.4998	0.866 00	−0.122	1.4504	68.43
0.1988	0.845 00	−0.109	1.4425	57.35	0.5905	0.871 08	−0.104	1.4522	71.76
0.2443	0.848 67	−0.119	1.4439	59.03	0.7005	0.876 66	−0.075	1.4542	75.80
0.3021	0.853 05	−0.130	1.4455	61.15	0.7914	0.880 89	−0.056	1.4560	79.17
0.3503	0.856 47	−0.131	1.4468	62.93	0.8957	0.885 33	−0.029	1.4578	83.04
0.3906	0.859 21	−0.134	1.4478	64.41	1.0	0.889 40		1.4590	86.82
$C_{12}H_{26}O$									
0.0	0.829 73		1.4410	59.30	0.4989	0.864 93	−0.094	1.4518	73.05
0.1019	0.838 15	−0.039	1.4437	62.12	0.5456	0.867 59	−0.094	1.4526	74.33
0.2025	0.845 78	−0.075	1.4457	64.85	0.6024	0.870 69	−0.085	1.4534	75.88
0.3012	0.852 65	−0.090	1.4480	67.60	0.6860	0.875 05	−0.076	1.4547	78.18
0.3473	0.855 70	−0.100	1.4491	68.89	0.7871	0.879 98	−0.052	1.4563	80.98
0.3945	0.858 68	−0.098	1.4500	70.19	0.8899	0.884 67	−0.024	1.4578	83.83
0.4490	0.861 99	−0.093	1.4510	71.69	1.0	0.889 40		1.4590	86.82

Experimental values of n_D for binary mixtures (Tables I and II) were fitted by the least-squares method with a polynomial function of the form

$$n_D = \sum_{i=1}^{n} A_i x^{i-1} \qquad (6)$$

where the values of coefficients A_i are listed in Table III along with the standard deviations, $s(n_D)$, of each fitting.

The refractive index for a pure liquid can be related to its molar volume V_m in terms of the molar refraction $[R]$ according to the Lorenz–Lorentz equation (7):

$$[R] = \frac{n^2 - 1}{n^2 + 2} V_m \qquad (7)$$

This can be rearranged for a binary mixture as

$$[R]_{12} = \frac{n_{12}^2 - 1}{n_{12}^2 + 2} \frac{M_{12}}{\rho_{12}} \qquad (8)$$

where subscript 12 refers to the binary mixture and M_{12} is the average molar mass defined as $x_1M_1 + (1 - x_1)M_2$. Values of $[R]_{12}$ are given in Tables I and II with an associated uncertainty of ±0.02 cm^3 mol^{-1}, by considering the uncertainties estimated for ρ and n_D.

In order to check the vality of the Lorenz–Lorentz equation to the experimental values, a plot of $[R]_{12}$ vs x_1 is shown in Figure 3. All binary mixtures fit eq 8 satisfactorily (regression coefficients, $r = 0.999$). On the other hand, $[R]_{12}$ is expected to be an additive and constitutive quantity for mixtures:

$$[R]_{12} = x_1[R]_1 + (1 - x_1)[R]_2 \qquad (9)$$

where subscripts 1 and 2 correspond to components 1 and 2. The difference between the experimental and predited values exceeds the experimental uncertainty of ±0.02 cm^3 mol^{-1} which can be adscribed to strong interactions between components 1 and 2.

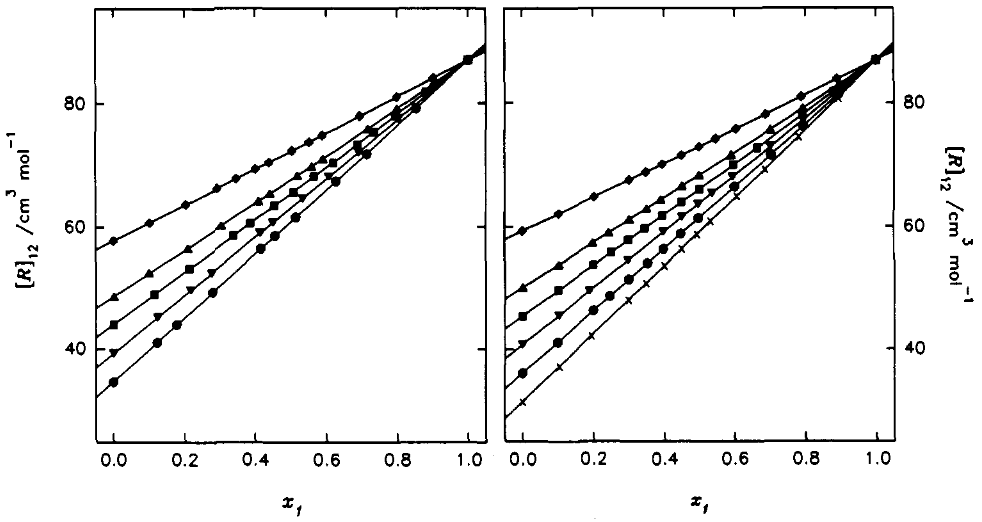

Figure 3. Molar refractions $[R]_{12}$ for *n*-alkanes and alkan-1-ols as a function of the oleic acid mole fraction x_1: (left side) ●, heptane; ▼, octane; ■, nonane; ▲, decane; ♦, dodecane; (right side) ×, hexan-1-ol; ●, heptan-1-ol; ▼, octan-1-ol; ■, nonan-1-ol; ▲, decan-1-ol; ♦, dodecan-1-ol.

Table III. Coefficients A_i and Standard Deviation s for Representation of Excess Molar Volumes V_m^E and Refractive Indices n_D for x $C_{18}H_{34}O_2$ + (1 − x) Organic Compound at 298.15 K by Equations 1 and 6

organic compound		A_1	A_2	A_3	A_4	10^3s	organic compound		A_1	A_2	A_3	A_4	10^3s
C_7H_{16}	$V_m^E/(cm^3\ mol^{-1})$	−3.3292	−1.3527	−0.7144		12.8	$C_7H_{16}O$	$V_m^E/(cm^3\ mol^{-1})$	−0.6118	−0.4176	−0.1105	−0.2365	3.22
	n_D	1.3860	0.1635	−0.1477	0.0575	0.103		n_D	1.4226	0.0793	−0.0686	0.0258	0.034
C_8H_{18}	$V_m^E/(cm^3\ mol^{-1})$	−2.7229	−0.8804			10.0	$C_8H_{18}O$	$V_m^E/(cm^3\ mol^{-1})$	−0.5190	−0.5083	−0.1604	0.2565	3.97
	n_D	1.3960	0.1230	−0.0899	0.0300	0.052		n_D	1.4277	0.0622	−0.0469	0.0160	0.022
C_9H_{20}	$V_m^E/(cm^3\ mol^{-1})$	−1.8564	−0.3919	−0.3740		17.0	$C_9H_{20}O$	$V_m^E/(cm^3\ mol^{-1})$	−0.5117	−0.3397	−0.0684		2.18
	n_D	1.4045	0.1021	−0.0750	0.0278	0.110		n_D	1.4319	0.0505	−0.0355	0.0125	0.001
$C_{10}H_{22}$	$V_m^E/(cm^3\ mol^{-1})$	−1.5070	−0.1898	−0.0691	0.4455	8.53	$C_{10}H_{22}O$	$V_m^E/(cm^3\ mol^{-1})$	−0.4860	−0.3194	−0.0583	0.0648	1.85
	n_D	1.4102	0.0811	−0.0481	0.0158	0.021		n_D	1.4355	0.0389	−0.0216	0.0063	0.039
$C_{12}H_{26}$	$V_m^E/(cm^3\ mol^{-1})$	−0.6094	−0.1553	−0.1501		5.51	$C_{12}H_{26}O$	$V_m^E/(cm^3\ mol^{-1})$	−0.3822	−0.1228			3.01
	n_D	1.4197	0.0567	−0.0234	0.0060	0.001		n_D	1.4410	0.0265	−0.0111	0.0026	0.016
$C_6H_{14}O$	$V_m^E/(cm^3\ mol^{-1})$	−0.6796	−0.5525	−0.3195		3.56							
	n_D	1.4164	0.0992	−0.0923	0.0358	0.058							

Literature Cited

(1) Maeda, H.; Eguchi, Y.; Suzuki, M. *J. Phys. Chem.* **1992**, *96*, 10487.
(2) Yanes, C.; Pérez-Tejeda, P.; Maestre, A. *J. Chem. Thermodyn.* **1989**, *21*, 819, 1217.
(3) Yanes, C.; Pellicer, J.; Rojas, E.; Zamora, M. *J. Chem. Thermodyn.* **1979**, *11*, 177.
(4) Yanes, C.; Pérez-Tejeda, P.; García-Pañeda, E.; Maestre, A. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 223.
(5) Zhao, V.; Hu, Y. *Fluid Phase Equilib.* **1990**, *57*, 89.
(6) Marsh, K. N. *Annu. Rep. Prog. Chem., Sect. C* **1990**, *77*, 101.
(7) Handa, Y. P.; Benson, G. C. *Fluid Phase Equilib.* **1979**, *3*, 185.
(8) Bottcher, C. J. F.; Bordewijk, P. *Theory of Electric Polarization*, 2nd ed.; Elsevier: Amsterdam, 1978; Vol. II, Chapter XII.

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