612 J. Chem. Eng. Data **1996,** *41,* 612−618

Densities, Speeds of Sound, Viscosities, Dielectric Constants, and Refractive Indices for 1-Heptanol + Hexane and +Heptane at 303.15 and 313.15 K

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New data on densities, speeds of sound, viscosities, dielectric constants, and refractive indices for the mixtures of 1-heptanol + hexane and +heptane at 303.15 and 313.15 K are reported. The excess volumes, V^E, and excess isentropic compressibilities, K_s^E, viscosity deviations, $\delta\eta$, dielectric constant deviations, $\delta\epsilon$, and molar and orientation polarization deviations, δP_m and δP_o, were calculated from the experimental data. The experimental speeds of sound have been analyzed in terms of free length theory (FLT) and collision factor theory (CFT). The experimental viscosities were also fitted to Grunberg−Nissan, McAllister, and Auslander equations.

Introduction

The binary mixtures of alcohol + alkanes have been studied extensively and systematically in recent years. The effect of alkyl chain length of both the components on the excess volumes, speeds of sound, and isentropic compressibilities has been studied by Treszczanowicz et al. (1978, 1980, 1981), Kiyohara and Benson (1979), Handa et al. (1981), and Benson and Halpin (1981). Treszczanowicz et al. (1993) have reviewed in detail the existing literature on the binary mixture data of excess molar volumes of 1-alkanol + alkanes and also recommended a few data sets. The influence of the alcohol chain length on excess molar enthalpies and excess molar heat capacities of 1-alkanol + alkane mixtures was also reviewed (Roux et al., 1993; Fernandez et al., 1990).

Attempts were also made to extend the thermodynamic studies to the measurements of viscosities of decanol + *n*-alkanes and alcohol + octane mixtures at 298.15 K by Bravo et al. (1991) and Franjo et al. (1995), respectively. Measurements of dielectric constants of alcohol + heptane mixtures were also previously reported (Glasser et al., 1972). A perusal of the literature on the alcohol + alkane mixtures revealed that the viscosities and dielectric constant measurements of alcohol + alkane systems are scarce. With an aim to carry out the systematic investigations involving the thermodynamic studies of alcohol + alkane mixtures through measurements of scarcely reported physical properties, this paper reports the new measurements of densities, speeds of sound, viscosities, dielectric constants, and refractive indices of 1-heptanol + hexane and +heptane at 303.15 and 313.15 K. The related excess functions were calculated from the measured properties of the mixture and pure components.

Experimental Section

Materials. 1-Heptanol, hexane, and heptane were of BDH AnalaR grade chemicals and used as such without any treatment. The purity of these chemicals was ascertained by comparing their measured densities (ρ), speeds of sound (v), viscosities (η), refractive indices (n), and the dielectric constants at different temperatures with the reported literature values, and such a comparison is presented in Table 1.

Table 1. Densities (ρ), Sound Velocities (v), Viscosities, Refractive Indices (n), and Dielectric Constants of Pure Liquids

	298.15 K		303.15 K		313.15 K	
	this work	lit.	this work	lit.	this work	lit.
Hexane						
ρ/g·cm^{-3}	0.6547	0.6548[a]	0.6502	0.6502[a]	0.6411	0.6414[l] 0.6413[o]
n	1.3723	1.3722[c]	1.3695	1.3698[a] 1.3699[d]	1.3675	1.3642[d]
v/m·s^{-1}	1076.3	1076.3[k] 1076.4[q]	1028.4	1028.6[m]	986.0	985.4[m]
η/mPa·s			0.2830	0.2831[b]	0.2582	0.2584[b]
ϵ			1.8711	1.8900[d]	1.8610	1.8790[d]
Heptane						
ρ/g·cm^{-3}	0.6794	0.6794[c]	0.6756	0.6754[a]	0.6660	0.6668[e]
n	1.3850	1.3851[c]	1.3830	1.3827[a]	1.3800	
v/m·s^{-1}	1129.5	1129.9[n]	1122.8		1101.2	
η mPa·s			0.3764	0.3707[b]	0.3351	0.3356[b]
ϵ			1.9020		1.8820	
1-Heptanol						
ρ/g·cm^{-3}	0.8187	0.8189[a] 0.8187[h] 0.8182[g]	0.8155	0.8154[a] 0.8157[h]	0.8084	0.8088[p]
n	1.4222	1.4222[g] 1.4223[a] 1.4221[i]	1.4205	1.4205[a]	1.4158	1.4160[h]
v/m·s^{-1}			1327.2	1310.4[j]	1282.4	
η/mPa·s			5.0100	4.9470[f]	3.6542	3.6880[f]
ϵ			10.8724	10.8763[i]	10.0201	9.9074[i]

[a] Ortega and Matos (1986). [b] TRC Tables (1992). [c] TRC Tables (1977). [d] Singh and Sinha (1982). [e] Goates et al. (1981). [f] Rauf et al. (1983). [g] Fernandez et al. (1985). [h] Ortega (1982). [i] Vij et al. (1978). [j] Chandrashekar et al. (1989). [k] Benson and Halpin (1986). [l] Riddick et al. (1986). [m] Zielkiewicz (1994). [n] Junquera et al. (1988). [o] Srinivasulu and Naidu (1990). [p] Diaz Pena and Tardajos (1979). [q] Benson and Halpin (1981).

Methods. Binary mixtures were prepared by mass on a single pan Mettler balance in stoppered glass bottles. The calculated mole fractions were accurate up to ±0.0001 units.

The densities of the mixture and pure components were measured by a precalibrated bicapillary pycnometer with an accuracy of ±0.0001 units. The temperature during the density measurements was controlled to an absolute precision of 0.01 °C.

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The speeds of sound in the pure liquids and their mixtures were measured with a single crystal Ultrasonic interferometer operating at a fixed frequency of 2 MHz. The temperature of the double jacketed interferometer cell was maintained by circulating the water from a thermostatic bath. The temperature in the interfermoter cell was maintained to a precision of 0.02 deg. The measured speeds of sound were accurate to ±0.15%. The isentropic compressibilities, K_s, were evaluated from the following relation:

$$K_s/(\mathrm{T{\cdot}Pa})^{-1} = 1/v^2\varrho \tag{1}$$

where v is the speed of sound in $\mathrm{m{\cdot}s^{-1}}$ and ρ is density in $\mathrm{kg{\cdot}m^{-3}}$.

The viscosities were calculated from the measured flow times, t, in an Ubbelhode suspended type viscometer by using the following relation:

$$\eta/\mathrm{mPa{\cdot}s} = \varrho/\mathrm{g{\cdot}cm^{-3}}\ \{At(s) - B/t(s)\} \tag{2}$$

where ρ is density and A and B are viscometer calibration constants which were preestimated from the measured flow times and densities of the triple-distilled water and double-distilled cyclohexane. The measured viscosities were found to be accurate up to ±0.003 mPa·s. The mixture viscosities were also mathematically represented by the following expressions:

$$\ln \eta_{12} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{3}$$

$$\ln \eta = x_1^3 \ln \eta_1 + 3x_1^2x_2(\ln M_{12}) + 3x_1x_2^2(\ln M_{21}) + x_2^3 \ln \eta_2 + 3x_1^2 \ln((2M_1 + M_2)/M_1) + 3x_2x_1^2 \ln((2M_2 + M_1)/M_1) + 3x_1x_2^2 \ln((3M_1 + 2M_2)/3M_1) - \ln(x_1 + (x_2M_2)/M_1) \tag{4}$$

and

$$x_1(x_1 + B_{12}x_2)(\eta_{12} - \eta_1) + A_{21}x_2(B_{21}x_1 + x_2)(\eta_{12} - \eta_2) = 0 \tag{5}$$

where G_{12}, M_{12}, M_{21}, A_{21}, B_{12}, and B_{21} are the adjustable parameters representing binary interactions. x_1, x_2, M_1, M_2, η_1, and η_2 are the mole fraction, molar mass, and viscosities of 1-heptanol (1) and alkane (2), respectively. Equations 3−5 are known as the Grunberg−Nissan, McAllister, and Auslander equations.

The dielectric constants were measured with a Universal dielectrometer (Type OH-301 of Radelkis, Hungary) at a fixed frequency of 3 MHz. The stainless steel cells were thermostated (±0.02 deg) by circulating the water from a constant temperature water bath. Measured dielectric constants were accurate up to ±0.0002 units.

Refractive indices for the sodium D line were measured with an Abbe Research refractometer. The measuring temperature was controlled by circulating the water from a thermostated water bath. Measured refractive indices were accurate up to ±0.0002 units.

Results

Table 2. Densities (ρ) and Excess Volume (V^E) of 1-Heptanol + Alkane Mixtures at 303.15 and 313.15 K

	303.15 K		313.15 K	
x_1	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}	ρ/g·cm^{-3}	V^E/cm^3·mol^{-1}
	1-Heptanol (1) + Hexane (2)			
0.0308	0.6555	0.033	0.6466	0.061
0.0919	0.6666	−0.036	0.6580	−0.059
0.1567	0.6785	−0.153	0.6700	−0.183
0.2496	0.6951	−0.264	0.6868	−0.312
0.4018	0.7216	−0.395	0.7134	−0.420
0.4831	0.7352	−0.402	0.7272	−0.440
0.5780	0.7508	−0.397	0.7429	−0.421
0.6838	0.7678	−0.366	0.7601	−0.388
0.7882	0.7839	−0.260	0.7765	−0.296
0.8946	0.8000	−0.146	0.7930	−0.209
0.9642	0.8103	−0.056	0.8035	−0.125
	1-Heptanol (1) + Heptane (2)			
0.0373	0.6804	0.090	0.6706	0.108
0.1040	0.6894	0.051	0.6795	0.078
0.1707	0.6986	0.010	0.6892	0.029
0.2845	0.7147	−0.088	0.7057	−0.104
0.4114	0.7325	−0.139	0.7238	−0.160
0.5113	0.7466	−0.169	0.7380	−0.162
0.6200	0.7619	−0.169	0.7537	−0.184
0.7301	0.7775	−0.161	0.7696	−0.175
0.8089	0.7885	−0.113	0.7809	−0.137
0.9029	0.8019	−0.087	0.7945	−0.092
0.9699	0.8113	−0.031	0.8042	−0.051

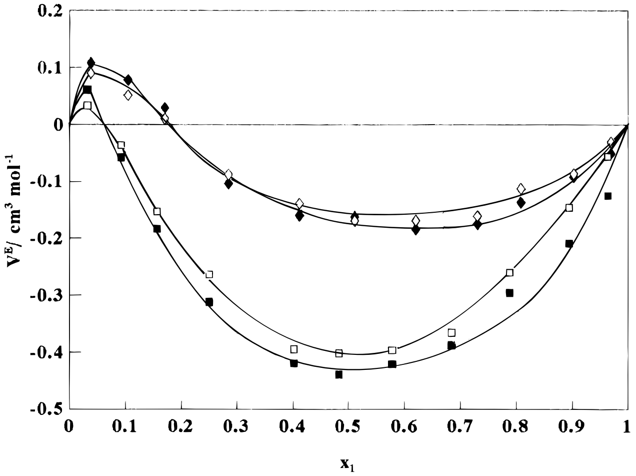

Figure 1. Excess volumes of 1-heptanol (1) + alkanes (2) versus 1-heptanol mole fraction at 303.15 K [(■) hexane, (◆) heptane] and at 313.15 K [(□) hexane, (◇) Heptane]. (—) Calculated from smoothing eq 6 by using coefficients from Table 3.

The experimental densities (ρ) and excess volumes, V^E, of the two binary mixtures of 1-heptanol + hexane and +heptane over the entire mole fraction range at 303.15 and 313.15 K are given in Table 2 and graphically presented in Figure 1. The V^E values were fitted to the following empirical equation:

$$V^E/\mathrm{cm^3{\cdot}mol^{-1}} = x_1(1 - x_1)\sum_{j=1} a_j x_1^{(j-1)/2} \tag{6}$$

where x_1 is the mole fraction of 1-heptanol and a_j are the adjustable coefficients. The values of these coefficients were obtained by a multiple regression analysis based upon a least squares method and are given in Table 3 together with the calculated standard deviation σ.

The experimental speeds of sound, v, isentropic compressibilities, K_s, and excess isentropic compressibilities, K_s^E of the two binary mixtures at 303.15 and 313.15 K are given in Table 4. The K_s^E values were calculated as

$$K_s^E = K_s - K_s^{id} \tag{7}$$

where K_s is the isentropic compressibility of the mixture and K_s^{id} is the isentropic compressibility of the ideal

Table 3. Coefficients a_i of Eq 6 with Standard Deviation, σ, for the Least Squares Representation of V^E of 1-Heptanol + Alkane Mixtures at 303.15 and 313.15 K

	$cm^3 \cdot mol^{-1}$				
T/K	a_1	a_2	a_3	a_4	σ
	1-Heptanol (1) + Hexane (2)				
303.15	−4.5560	−25.2146	33.4779	−14.4694	0.001
303.15	−9.2683	−55.7234	91.1975	−48.2263	0.001
	1-Heptanol (1) + Heptane (2)				
303.15	7.1501	−32.1482	44.4189	−20.5887	0.001
303.15	8.9247	−40.9511	59.0621	−28.6926	0.001

Table 4. Volume Fraction, ϕ_1, of 1-Heptanol, Speed of Sound, v, Isentropic, Compressibility, K_s, and Excess Isentropic Compressibilities, K_s^E, Computed from Eq 7 for 1-Heptanol + Alkane Mixtures at 303.15 K and 313.15 K

	303.15 K				313.15 K		
ϕ_1	v/m·s^{-1}	K_s/ T·Pa^{-1}	K_s^E/ T·Pa^{-1}	ϕ_1	v/m·s^{-1}	K_s/ T·Pa^{-1}	K_s^E/ T·Pa^{-1}
			1-Heptanol (1) + Hexane (2)				
0.0330	1034	1427	−5	0.0329	992	1572	−5
0.0981	1050	1361	−25	0.0977	1004	1508	−16
0.1665	1067	1295	−41	0.1658	1016	1447	−27
0.2634	1092	1206	−60	0.2625	1041	1344	−43
0.4193	1136	1074	−76	0.4181	1082	1198	−58
0.5012	1161	1009	−79	0.5000	1107	1122	−64
0.5956	1191	939	−77	0.5944	1137	1042	−63
0.6993	1227	865	−71	0.6982	1172	958	−58
0.8000	1265	797	−61	0.7993	1211	878	−50
0.9012	1300	740	−38	0.9008	1248	810	−30
0.9666	1319	709	−18	0.9665	1270	772	−10
			1-Heptanol (1) + Heptane (2)				
0.0359	1128	1156	−5	0.0357	1103	1226	−4
0.1033	1139	1118	−13	0.0998	1115	1184	−12
0.1651	1151	1080	−24	0.1643	1125	1146	−22
0.2764	1175	1013	−41	0.2753	1143	1085	−32
0.4030	1201	946	−50	0.4016	1164	1020	−38
0.5013	1223	895	−53	0.4987	1181	971	−40
0.6105	1247	844	−52	0.6092	1204	915	−41
0.7221	1273	794	−47	0.7210	1232	856	−38
0.8026	1292	760	−41	0.8018	1245	826	−32
0.8993	1313	723	−29	0.8988	1266	785	−22
0.9687	1320	707	−10	0.9685	1281	758	−7

solution which was calculated by following relation:

$$K_s^{id} = \sum_i \phi_i\{K_{s,i} + TV_i(\alpha_i)^2/C_{p,i}\} - T(\sum x_iV_i)(\sum \phi_i\alpha_i)^2/(\sum_i x_iC_{p,i}) \quad (8)$$

where T is the temperature, x_i is the mole fraction of the component i in the mixture, and $K_{s,i}$, V_i, α_i, and $C_{p,i}$ are the isentropic compressibility, molar volume, isobaric thermal expansivity, and molar heat capacities for the pure components. ϕ_i is the ideal volume fraction of component i in the mixture and is defined by the relation

$$\phi_i = x_iV_i/(\sum x_iV_i)$$

The values of α_i and V_i were calculated from the measured densities, and the molar heat capacities of alkanes were interpolated from the literature data of Messerly et al. (1967). The heat capacities of 1-heptanol were evaluated from the isothermal compressibilities reported by Diaz Pena and Tardajos (1979).

The speeds of sound of the two binary mixtures at 303.15 K were also evaluated from both free length theory (FLT) and collision factor theory (CFT) formulations. The pertinent relations in these calculations and their theoretical basis were described by Jacobson (1952), Nutsch-Kuhnkies (1965), and Schaffs (1963). The surface area, Y, and collision factor, S, of the pure components used in FLT and CFT calculations were estimated by using the experimental speeds of sound and molar volumes. The data of molar volume, V_m, molar volume at absolute zero, V_0, available volume, V_a, free length, L_f, surface area, Y, collision factor, S, and molecular radius, r_j, of the pure components are given in Table 5. The FLT and CFT calculated speed of sound data together with the percentage deviation between experimental and theoretical values are included in columns 3−6 of Table 6.

The K_s^E values of the mixtures were mathematically represented by a Redlich−Kister type equation,

$$K_s^E/T\cdot Pa^{-1} = x_1(1 - x_1)\sum_{i=0} a_i(2x_1 - 1)^i \quad (9)$$

where x_1 is the 1-heptanol mole fraction and a_i are the coefficients. The values of a_i were calculated by a least squares method and are given in Table 7 together with the standard deviation σ. The experimental K_s^E values of binary mixtures are also depicted graphically as a function of 1-heptanol mole fraction at both 303.15 and 313.15 K in Figure 2.

The measured viscosities, η_{exp}, and viscosity deviation, $\delta\eta$, for 1-heptanol + alkane mixtures are given as a function of mole fraction at both the temperatures in Table 8. The viscosity deviation, $\delta\eta$, was calculated from the following relation:

$$\delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (10)$$

The values of the viscosity deviations were also fitted through eq 9 and are graphed as a function of 1-heptanol mole fraction in Figure 3. The values of the coefficients for fittings of viscosity deviation, estimated by least squares analysis are given in Table 9. The experimental viscosities and viscosity increment ratios of the binary mixtures were further fitted to the Grunberg−Nissan, McAllister, and Auslander equations, eqs 3−5. The respective adjustable parameters that appear in eqs 3−5 were estimated using the experimental viscosity data and a nonlinear regression analysis employing the Marquardt alogarithm based upon a least squares method. Values of the adjustable parameters of the three equations for the binary mixtures at both the temperatures, along with the standard deviation between the experimental and calculated viscosities, are given in Table 10. Examination of Table 10 shows that the σ values for the three equations in general were found to lie between 0.001 and 0.005, indicating the suitability of all three relations for representing the mixture viscosities of alcohol + alkanes.

The dielectric constants (ϵ), refractive indices (n), dielectric constant deviations, $\delta\epsilon$, refractive index deviations, δn, molar polarization deviations, δP_m, and orientation polar-

Table 5. Values of Molar Volume, V_m, Molar Volume at Absolute Zero, V_0, Available Volume, V_a, Free Length, L_f, Surface Area, Y, Collision Factor, S, and Molecular Radius, r_j of the Pure Components at 303.15 K

component	V_m/cm^3·mol^{-1}	V_0/cm^3·mol^{-1}	V_a/cm^3·mol^{-1}	L_f/Å	Y	S	r_j/Å
hexane	132.532	100.879	31.653	0.7449	84.986	2.5713	2.359
heptane	148.310	115.848	32.462	0.6740	96.312	2.8059	2.450
1-heptanol	142.489	117.180	25.309	0.5282	95.831	3.3177	2.417

Table 6. Values of Free Lengths of Mixtures, L_f^M, Experimental and Predicted Speeds of Sound, v, for the 1-Heptanol + Alkane Mixtures at 303.15 K

		v/m·s^{-1}			% Δv	
x_1	L_f^M/Å	exp	FLT	CFT	FLT	CFT
		1-Heptanol (1) + Hexane (2)				
0.0308	0.7382	1034	1034	1037	0	0.29
0.0919	0.7219	1050	1050	1056	0	0.57
0.1567	0.7038	1067	1069	1076	0.19	0.84
0.2496	0.6798	1092	1096	1105	0.40	1.19
0.4018	0.6436	1136	1140	1151	0.35	1.32
0.4831	0.6248	1161	1166	1176	0.43	1.29
0.5780	0.6047	1191	1195	1204	0.34	1.09
0.6838	0.5833	1227	1227	1236	0	0.73
0.7882	0.5643	1265	1258	1266	−0.55	0.08
0.8946	0.5456	1300	1291	1297	−0.69	−0.23
0.9642	0.5339	1319	1313	1317	−0.45	−0.15
		1-Heptanol (1) + Heptane (2)				
0.0373	0.6705	1128	1124	1130	−0.35	0.18
0.1040	0.6600	1139	1136	1144	−0.26	0.44
0.1707	0.6495	1151	1148	1157	−0.26	0.52
0.2845	0.6309	1175	1170	1182	−0.43	0.60
0.4114	0.6114	1201	1195	1208	−0.50	0.58
0.5113	0.5962	1223	1216	1229	−0.57	0.33
0.6200	0.5803	1247	1239	1251	−0.64	0.32
0.7301	0.5644	1273	1262	1273	−0.86	0
0.8089	0.5539	1292	1280	1291	−0.93	0.10
0.9029	0.5406	1313	1302	1308	−0.84	−0.38
0.9699	0.5320	1320	1317	1321	−0.23	0.10

Table 7. Coefficients a_i of Eq 8 with Standard Deviation, σ, for the Least Squares Representation of K_s^E of 1-Heptanol + Alkane Mixtures at 303.15 and 313.15 K

	T·Pa^{-1}				
T/K	a_0	a_1	a_2	a_3	σ
	1-Heptanol (1) + Hexane (2)				
303.15	−320.935	65.416	−43.989	−268.157	0.40
313.15	−257.924	−61.462	20.471	−10.452	0.40
	1-Heptanol (1) + Heptane (2)				
303.15	−210.645	−40.888	−32.705	−89.614	0.40
313.15	−167.509	−32.070	−20.058	−47.412	0.40

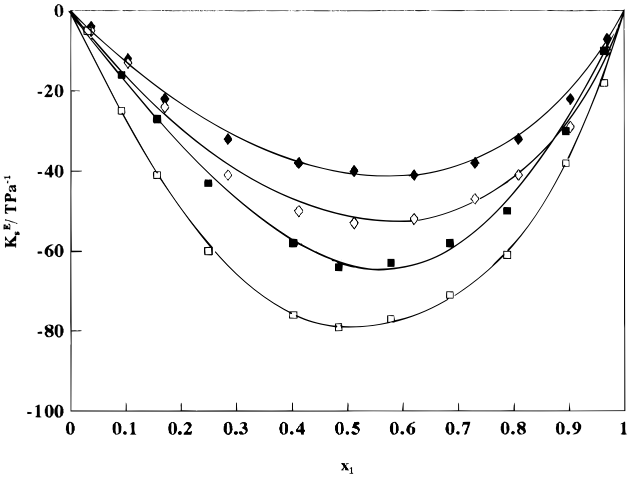

Figure 2. Excess isentropic compressibilities of 1-heptanol (1) + alkanes (2) versus 1-heptanol mole fraction at 303.15 K [(■) hexane, (♦) heptane] and at 313.15 K [(□) hexane, (◇) heptane]. (—) Calculated from smoothing eq 9 by using coefficients from Table 7.

ization deviations, δP_o, are presented in Table 11. The deviations in various dielectric functions, viz. $\delta\epsilon$, δn, δP_m, and δP_o, from the ideal value, assumed to be additive in terms of mole fraction, are estimated by using the following general equation:

$$\delta A = A - \sum(x_i A_i) \tag{11}$$

where A and A_i are the respective dielectric functions of the mixture and pure components and x_i is the mole fraction of the respective pure components. The molar polarizations and orientation polarizations were calculated from the standard relations using the pure component data.

The data of $\delta\epsilon$, δP_m, and δP_o are also fitted through eq 5. The values of the fitting coefficients along with the standard deviations, σ, for the individual functions at both the temperatures are given in Table 12. The variation of $\delta\epsilon$ and δP_m over the entire range of 1-heptanol mole fraction is also presented in Figures 4 and 5, respectively, for both the mixtures at 303.15 and 313.15 K.

Discussion

The dependence of V^E on the 1-heptanol mole fraction, as given in Figure 1, is typical and follows a trend similar

Table 8. Experimental Viscosities (η_{exp}), Calculated Viscosites (η_{cal}), and Viscosity Deviations ($\delta\eta$) of 1-Heptanol + Alkane Mixtures at 303.15 K and 313.15 K

	303.15 K				313.15 K			
x_1	η_{exp}/mPa·s	η_{cal}(eq 3)/mPa·s	η_{cal}(eq 3)/mPa·s	$\delta\eta$/mPa·s	η_{exp}/mPa·s	η_{cal}(eq 3)/mPa·s	η_{cal}(eq 3)/mPa·s	$\delta\eta$/mPa·s
				1-Heptanol (1) + Hexane (2)				
0.0308	0.2866	0.3028	0.3007	−0.142	0.2693	0.2741	0.2746	−0.093
0.0919	0.3254	0.3477	0.3419	−0.392	0.2940	0.3097	0.3111	−0.276
0.1567	0.3966	0.4050	0.3959	−0.627	0.3446	0.3547	0.3569	−0.446
0.2496	0.5095	0.5090	0.4971	−0.953	0.4493	0.4357	0.4386	−0.657
0.4018	0.7642	0.7597	0.7507	−1.418	0.6611	0.6270	0.6291	−0.962
0.4831	0.9566	0.9533	0.9512	−1.611	0.7663	0.7724	0.7728	−1.133
0.5780	1.2479	1.2573	1.2691	−1.767	0.9882	0.9975	0.9949	−1.233
0.6838	1.7760	1.7372	1.7718	−1.739	1.3480	1.3476	1.3403	−1.232
0.7882	2.4788	2.4269	2.4853	−1.530	1.8319	1.8428	1.8311	−1.103
0.8946	3.5219	3.4656	3.5304	−0.990	2.4733	2.5780	2.5649	−0.823
0.9642	4.3837	4.4218	4.4482	−0.458	3.1745	3.2398	3.2330	−0.358
				1-Heptanol (1) + Heptane (2)				
0.0373	0.4020	0.4058	0.3716	−0.147	0.3519	0.3594	0.3628	−0.107
0.1040	0.4690	0.4660	0.4445	−0.389	0.4152	0.4087	0.4178	−0.265
0.1707	0.5430	0.5382	0.5289	−0.625	0.4918	0.4671	0.4807	−0.410
0.2845	0.7030	0.6963	0.7053	−0.992	0.6087	0.5930	0.6108	−0.671
0.4114	0.9010	0.9451	0.9670	−1.382	0.7971	0.7865	0.8026	−0.903
0.5113	1.2100	1.2184	1.2400	−1.536	0.9558	0.9944	0.9631	−1.076
0.6200	1.6710	1.6281	1.6385	−1.578	1.3180	1.2993	1.2912	−1.075
0.7301	2.2360	2.2151	2.2027	−1.523	1.6815	1.7255	1.6962	−1.077
0.8089	2.8010	2.7860	2.7544	−1.324	2.0821	2.1308	2.0901	−0.938
0.9029	3.7416	3.6980	3.6557	−0.818	2.7276	2.7646	2.7220	−0.604
0.9699	4.5534	4.5544	4.5317	−0.317	3.3220	3.3478	3.3254	−0.232

Table 9. Coefficients of Eq 9 Together with the Standard Deviations (σ) for the Least Squares Representations of Viscosity Deviations, $\delta\eta$, of 1-Heptanol + Alkane Mixtures at 303.15 K and 313.15 K

	mPa·s			
T/K	a_0	a_1	a_2	σ
	1-Heptanol (1) + Hexane (2)			
303.15	−6.3704	−4.0858	−2.6164	0.001
313.15	−4.4311	−3.4901	−2.5636	0.001
	1-Heptanol (1) + Heptane (2)			
303.15	−5.9820	−3.3654	−1.4931	0.001
313.15	−4.0372	−2.5488	−1.4623	0.001

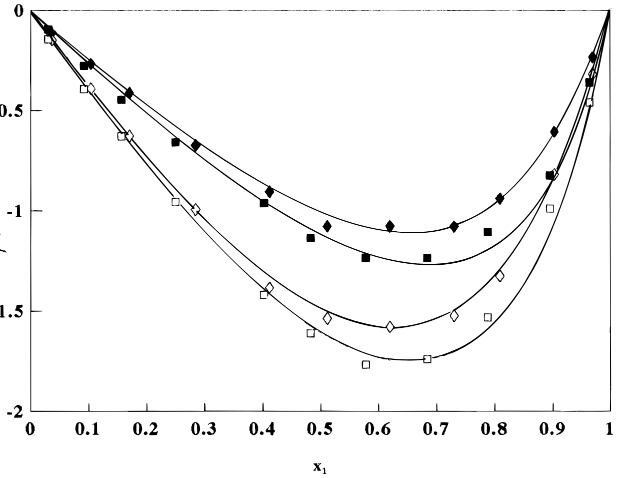

Figure 3. Viscosity deviations of 1-heptanol (1) + alkanes (2) versus 1-heptanol mole fraction at 303.15 K [(■) hexane, (♦) heptane] and at 313.15 K [(□) hexane, (◇) heptane]. (—) Calculated from smoothing eq 9 by using coefficients from Table 9.

to those of the other alcohol + alkane mixtures reported in the literature. The curves are asymmetrical in nature with an initial positive region followed by skewed negative lobes at alcohol rich regions. To our knowledge, there is no direct data on V^E for 1-heptanol + hexane and +heptane mixtures at 303.15 and 313.15 K in the literature for a direct comparison. However, relative comparisons between our data and those of either lower or higher alcohol + hexane and +heptane mixtures reported in the literature can be made. For example our value of $V^E_{0.5} = -0.405$ for 1-heptanol + hexane at 303.15 K is observed to lie between the $V^E_{0.5} = -0.2203$ (Treszczanowicz et al., 1980) or $V^E_{0.5} = -0.2275$ (Wagner, 1986) of 1-hexanol + hexane and $V^E_{0.5} = -0.5911$ (Treszczanowicz et al., 1981) of 1-decanol + hexane mixtures at 298.15 K. Similarly, our value of $V^E_{0.5} = -0.1671$ for 1-heptanol + heptane is found to be between $V^E_{0.5} = -0.0250$ and $V^E_{0.5} = -0.2148$ (Treszczanowicz et al., 1978) of 1-hexanol + heptane and 1-octanol + heptane mixtures at 298.15 K, respectively. Our observed temperature coefficients, $(\partial V^E/\partial T)_{0.5}$, of −0.003 37 and −0.000 58 for 1-heptanol + hexane and 1-heptanol + heptane mixtures, respectively, are similar in sign to those reported by Wagner et al. (1986) for several alcohol + alkane mixtures.

The excess isentropic compressibilities were observed to be negative over the entire range of 1-heptanol mole fraction (Figure 2). The K_s^E values for 1-heptanol +

Table 10. Adjustable Parameters of Eqs 3−5 with Standard Deviation σ for 1-Heptanol + Alkane Mixtures at 303.15 and 313.15 K

1-heptanol +	G_{12}	σ	M_{12}	M_{21}	σ	A_{21}	B_{21}	B_{12}	σ
				303.15 K					
hexane	−0.6956	0.003	1.6623	0.5415	0.004	0.3352	12.126	-0.0900	0.001
heptane	−0.5959	0.003	1.6269	0.8528	0.006	1.2975	2.6829	0.0430	0.005
				313.15 K					
hexane	−0.7386	0.004	1.1592	0.5025	0.004	0.6686	6.5950	0.0448	0.004
heptane	−0.5358	0.003	1.2825	0.6859	0.008	2.1860	1.6254	0.3580	0.002

Table 11. Dielectric Constants (ϵ), Refractive Indices (n), Dielectric Constant Deviations ($\delta\epsilon$), Refractive Indices Deviations (δn), Molar Polarization Deviations (δP_m), and Orientation Polarization Deviations (δP_o) of 1-Heptanol + Alkane Mixtures at 303.15 K and 313.15 K

	303.15 K						313.15 K					
x_1	ϵ	n	$\delta\epsilon$	δn	δP_m/cm³·mol⁻¹	δP_o/cm³·mol⁻¹	ϵ	n	$\delta\epsilon$	δn	δP_m/cm³·mol⁻¹	δP_o/cm³·mol⁻¹
					1-Heptanol (1) + Hexane (2)							
0.0308	1.9112	1.3709	−0.237	−0.0002	−1.3	−4.5	1.8987	1.3653	−0.214	−0.0003	−1.3	−4.1
0.0919	2.0237	1.3736	−0.675	−0.0006	−3.2	−12.6	1.9191	1.3682	−0.692	−0.0006	−5.4	−13.9
0.1567	2.1962	1.3768	−1.085	−0.0007	−4.1	−19.8	2.0536	1.3720	−1.086	−0.0001	−6.9	−21.1
0.2496	2.6080	1.3817	−1.510	−0.0005	−2.6	−26.6	2.3847	1.3778	−1.513	0.0009	−6.3	−28.2
0.4018	3.6732	1.3901	−1.815	0.0001	2.4	−30.5	3.2672	1.3863	−1.872	0.0015	−2.0	−33.1
0.4831	4.3941	1.3945	−1.826	0.0004	4.5	−30.4	3.8694	1.3906	−1.933	0.0016	0.1	−33.7
0.5780	5.3030	1.3998	−1.771	0.0008	5.5	−29.5	4.6661	1.3954	−1.911	0.0015	1.6	−33.1
0.6838	6.4520	1.4051	−1.574	0.0007	5.5	−26.6	5.6945	1.4006	−1.746	0.0012	2.4	−30.3
0.7882	7.7500	1.4100	−1.216	0.0003	4.5	−20.6	6.9163	1.4005	−1.476	0.0007	2.5	−24.0
0.8946	9.1206	1.4153	−0.803	0.0002	2.3	−13.9	8.2045	1.4106	−0.956	0.0003	1.0	−17.0
0.9642	10.1607	1.4187	−0.390	0.00003	0.6	−6.9	9.3322	1.4141	−0.396	0.0002	0.3	−7.2
					1-Heptanol (1) + Heptane (2)							
0.0373	1.9435	1.3841	−0.293	−0.0003	−1.6	−5.5	1.8820	1.3811	−0.304	−0.0002	−2.8	−6.2
0.1040	2.0460	1.3868	−0.789	−0.0001	−3.9	−14.7	1.8940	1.3834	−0.834	−0.0003	−7.4	−17.1
0.1707	2.2217	1.3898	−1.212	−0.0004	−4.5	−21.6	1.9057	1.3860	−1.365	−0.0001	−12.1	−27.9
0.2845	2.5271	1.3950	−1.927	0.0013	−6.2	−34.1	2.1450	1.3904	−2.052	0.0002	−14.1	−40.0
0.4114	3.3143	1.4000	−2.278	0.0016	−1.7	−38.0	2.8555	1.3952	−2.374	0.0005	−8.1	−42.6
0.5113	4.1560	1.4037	−2.333	0.0015	1.8	−37.7	3.6152	1.3991	−2.428	0.0008	−3.5	−41.7
0.6200	5.2504	1.4075	−2.213	0.0012	4.0	−35.1	4.5169	1.4032	−2.411	0.0010	−1.0	−40.6
0.7301	6.5946	1.4113	−1.857	0.0009	4.6	−32.1	5.6889	1.4070	−2.134	0.0009	0.7	−35.6
0.8089	7.7464	1.4139	−1.412	0.0006	4.4	−21.8	6.6443	1.4096	−1.821	0.0006	0.8	−30.4
0.9029	9.1190	1.4172	−0.882	0.0003	2.4	−13.8	8.0255	1.4126	−1.204	0.0003	0.4	−20.1
0.9699	10.2048	1.4195	−0.398	0.0001	0.5	−6.5	9.3208	1.4148	−0.454	0.0001	0.1	−7.7

Table 12. Coefficients of Eq 9 with Standard Deviation σ for the Least Squares Representation of $\delta\epsilon$, δn, δP_m, and δP_o of 1-Heptanol + Alkane Mixtures at 303.15 K and 313.15 K

	303.15 K					313.15 K				
	a_0	a_1	a_2	a_3	σ	a_0	a_1	a_2	a_3	σ
					1-Heptanol (1) + Hexane (2)					
$\delta\epsilon$	−7.162	1.962	−2.457	−4.129	0.0004	−7.797	0.526	−2.008	−3.098	0.0004
δn	0.0017	0.0051	−0.0057		0.00004	0.0069	−0.0015	−0.0122	0.01020	0.00001
δP_m/cm^3·mol^{-1}	16.979	36.663	−36.370		0.04	−2.079	60.618	−26.623	−32.911	0.04
δP_o/cm^3·mol^{-1}	−119.571	39.849	−57.966	−72.090	0.04	−135.760	31.791	−49.604	−75.484	0.04
					1-Heptanol (1) + Heptane (2)					
$\delta\epsilon$	−9.081	1.387	−1.184	−4.638	0.0004	−9.863	−0.113	−2.341	−4.252	0.0004
δn	0.0069	−0.005	−0.0101	0.012	0.0002	0.0034	0.0038	−0.0051	0.0011	0.0001
δP_m/cm^3·mol^{-1}	3.494	64.342	−18.241	−35.356	0.20	−24.444	89.302	−19.738	−52.754	0.04
δP_o/cm^3·mol^{-1}	−149.816	38.217	−28.372	−79.339	0.20	−174.075	34.893	−50.978	−95.594	0.10

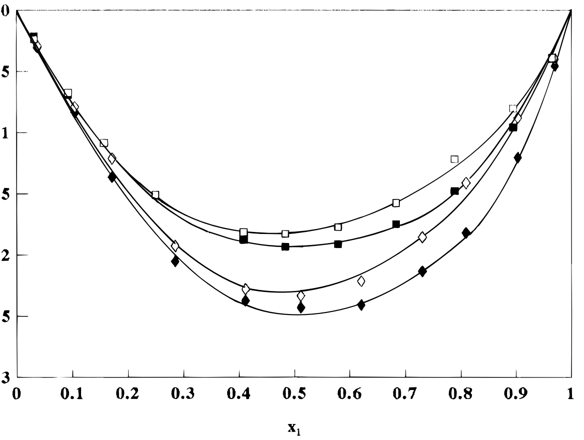

Figure 4. Dielectric constant deviations of 1-heptanol (1) + alkanes (2) versus 1-heptanol mole fraction at 303.15 K [(■) hexane, (♦) heptane] and at 313.15 K [(□) hexane, (◊) heptane]. (—) Calculated from smoothing eq 9 by using coefficients from Table 12.

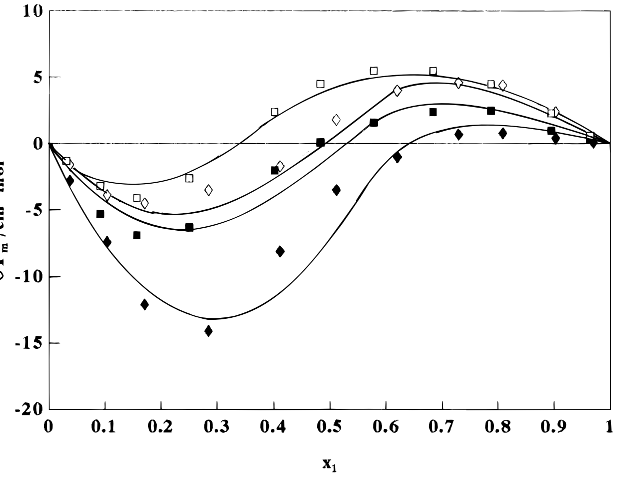

Figure 5. Molar polarization deviations of 1-heptanol (1) + alkanes (2) versus 1-heptanol mole fraction at 303.15 K [(■) hexane, (♦) heptane] and at 313.15 K [(□) hexane, (◊) heptane]. (—) Calculated from smoothing eq 9 by using coefficients from Table 12.

hexane mixtures were found to be less than those of 1-heptanol + heptane mixtures at both the temperatures. An increase in temperature results in a marginal increase in the compressibility. Our $K^{E}_{s\,0.5}$ value of −64.4 of 1-heptanol + hexane at 303.15 K is found to be between the excess compressibilities of −56.48 and −87.91 for 1-hexanol + hexane (Handa et al., 1981) and 1-decanol + hexane (Benson and Halpin, 1981) mixtures at 298.15 K, respectively. However, the $K^{E}_{s\,0.5}$ from our measurements on 1-heptanol + heptane at 303.15 K is found to be more negative than $K^{E}_{s\,0.5} = -25.0$ (Kiyohara and Benson, 1979) for 1-hexanol + hexane mixtures at 298.15 K. The temperature coefficient, $(\partial K^{E}_{s}/\partial T)_{0.5}$, for 1-heptanol + hexane and +heptane was found to be 0.911 and 0.891, respectively.

The initial positive V^{E} values in very dilute alcohol regions can be attributed to the breaking of the hydrogen bonding in alcohol molecules by unlike alkane species and the dipole−dipole interactions between the dissociated monomer and associated alcohol molecules. The negative excess volumes in alcohol rich regions can be explained as a result of the interstitial accommodation of alkane molecules into the branched alcohol associated structures and the accompanying free volume changes upon mixing.

The $\delta\eta$ values are in general negative and large over the entire range of 1-heptanol mole fraction (Figure 3). The curves are skewed toward the alcohol rich regions. An increased temperature is found to enhance the mixture viscosity contribution to the overall viscosity deviations. The large negative viscosity deviations suggest that in these mixtures, the forces between pairs of unlike molecules is less than the forces between like molecules.

The ϵ^{E} values are found to be negative over the entire range of composition. It can also further be noticed from Figure 4 that the initial ϵ^{E} values for both mixtures and at both temperatures were close to each other, suggesting that a slight increase in the carbon chain length and temperature seems to have little effect in the lower alcohol mole fraction regions. However, in contrast, appreciable changes were noted above a certain alcohol mole fraction of $x_1 \approx 0.15-0.20$. The ϵ^{E} values in this region were found to be more negative in 1-heptanol + heptane than in 1-heptanol + hexane mixtures. A slight decrease in the magnitude was noted with increasing the temperature in both mixtures in this region. The curves tend to be symmetrical at about equimole fractions. The negative $\delta\epsilon$ values can be ascribed to the changed orientation in the dipoles of 1-heptanol molecules due to the dipole−dipole interactions between its multimer and monomer species in the presence of alkane molecules, especially in the alcohol deficient regions.

The dependence of δP_m on the mole fraction of 1-heptanol, as can be seen from Figure 5, is sigmoidal in shape with initial steep negative lobes, followed by the positive regions at higher alcohol mole fractions. The negative δP_m values in the lower alcohol mole fraction range indicate the decreased polarization in the alcohol molecules which tends to support the earlier observation that repulsive dipole−dipole interactions are dominant in this region. The positive δP_m values at higher 1-heptanol mole fractions indicate the presence of larger proportion of ordered hydrogen-bonded structures, which leads to the contraction of volume. The excess orientation polarizations, δP_o, for these binary mixtures (Table 11) were, however, negative over the entire 1-heptanol mole fraction range, indicating the larger changes in the orientation of dipoles in alcohol molecules in mixtures than in the pure state.

Acknowledgment

The authors wish to thank the late Prof. Dr. M. N. Patel, ex-head of the department, for his encouragement and support.

Literature Cited

Benson, G. C.; Halpin, Y. P. Ultrasonic Speeds and isentropic Compressibilities for (Decan-1-ol + n-Alkane) at 298.15 K. *J. Chem. Thermodyn.* **1981**, *13*, 887−896.

Benson, G. C.; Halpin, C. J.; Kumaran, M. J. Ultrasonic Speeds and Isentropic Compressibilities of each of the Mixtures (n-Decane + an Isomer of Hexane) at 298.15 K. *J. Chem. Thermodyn.* **1986**, *18*, 1147−1152.

Bravo, R.; Pintos, M.; Amigo, A.; Garcia, M. Densities and Viscosities of Binary Mixtures of Decanol + Some n-Alkanes at 298.15 K. *Phys. Chem. Liq.* **1991**, *22*, 245−255.

Chandrashekar, A. C. H.; Ramanjaneyulu, K.; Krishnaiah, A. Volumetric and Ultrasonic Behaviour of Acetophenone and Alcohol Mixtures. *Phys. Chem. Liq.* **1989**, *19*, 171−179.

Diaz Pena, M.; Tardajos, G. Isothermal Compressibilities of n-Alcohols from Methanol to Decanol at 298.15, 308.15, 318.15 and 333.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 441−445.

Fernandez, J.; Legido, J. L.; Paz Andrade, M. I.; Pias, L. Analysis of Thermodynamic Properties of 1-Akanol n-Alkane Mixtures Using the Nitta-Chao Group Contribution Model. *Fluid Phase Equilib.* **1990**, *55*, 293−308.

Fernandez, J.; Pintos, M.; Baluja, M. C.; Jimenez, E.; Paz Andrade, M. I. Excess Enthalpies of Some Ester Alcohol Binary Mixtures. *J. Chem. Eng. Data* **1985**, *30*, 318−320.

Franjo, C.; Menaut, C. P.; Jimenez, E.; Legido, J. L.; Paz Andrade, M. I. Viscosities and Densties of Octane + Butan-1-ol, Hexan-1-ol, and Octan-1-ol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 992−994.

Glasser, L.; Crossley, J.; Smyth, C. P. The Absorption and Molecular Structure in Liquids. LXXIX. Dielectric Behaviour and Association of some n-Alcohols in n-Heptane Solutions. *J. Chem. Phys.* **1972**, *57*, 3977−3986.

Goates, J. B.; Ott, J. B.; Grigg, R. B. Excess Volumes of n-Hexane, + n-Heptane, n-Octane, + n-Nonane and n-Decane at 283.15, 298.15 and 313.15 K. *J. Chem. Thermodyn.* **1981**, *13*, 907−913.

Handa, Y. P.; Halpin, C. J.; Benson, G. C. Ultrasonic Speeds and Isentropic Compressibilities for (Decan-1-ol + n-Alkane) at 298.15 K. *J. Chem. Thermodyn.* **1981**, *13*, 887−896.

Jacobson, B. Intramolecular Free Lengths in The Liquid State. I. Adiabatic and Isothermal Compressibilities. *Acta. Chem. Scand. A* **1952**, *8*, 1485−1498.

Junquera, E.; Tardajos, G.; Aicart, E. Speeds of Sound and Isentropic Compressibilities of (Cyclohexane + Benzene) and (1-Chlorobutane + n-Hexane, or n-Heptane, or n- Octane or n-Decane) at 298.15 K. *J. Chem. Thermodyn.* **1988**, *20*, 1461−1467.

Kiyohara, O.; Benson, G. C. Ultrasonic Speeds and Isentropic Compressibilities of n-Alkanol + n-Heptane Mixtures at 298.15 K. *J. Chem. Thermodyn.* **1979**, *11*, 861−873.

Nutsch-Kuhnkies, R. Sound Velocities of Binary Mixtures and Solutions. *Acoustica* **1965**, *15*, 383−386.

Ortega, J. Densities and Refractive Indices of Pure Alcohols as a Function of Temperature. *J. Chem. Eng. Data* **1982**, *27*, 312−317.

Ortega, J.; Matos, J. S. Estimation of of Isobaric Expansivities from Several Equations of Molar Refraction for Some Pure Organic Compounds. *Mater. Chem. Phys.* **1986**, *15*, 415−425.

Ortega, J.; Gonzalez, E. Excess Molar Volumes of n-Hexane with Some Hexanol Isomers at 298.15 K. *Thermochim. Acta* **1993**, *217*, 301−308.

Rauf, M. A.; Stewart, G. H.; Farhataziz, J. Viscosities and Densities of Binary Mixtures of 1- Alkanols from 15 to 55 °C *J. Chem. Eng. Data* **1983**, *28*, 324−328.

Riddick, J. A.; Bunger, W.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of Chemistry; Wiley: New York, 1986.

Roux, A. H.; Roux-Desgranges, G.; Grolier, J. P. E. Excess Heat Capacities and Molar Enthalpies for 1-Alkanol + n-Alkane Binary Mixtures. New Measurements and Recommended Data. *Fluid Phase. Equilib.* **1993**, *89*, 57−88.

Schaffs, W. *Molekularakustich*; Springer Verlag: Berlin, 1963; Chapters XI and XII.

Singh, R. D.; Sinha, C. P. Dielectric Behavior of Binary Mixtures of *n*-Hexane with Toluene, Chlorobenzene, and 1-Hexanol. *J. Chem. Eng. Data* **1982**, *27*, 283−287.

Srinivasulu, U.; Naidu, P. R. Excess Volumes for Ternary Mixtures Containing 1,1,1-Tricloromethane + *n*-Hexane with 1-Propanol, 1-Butanol, and 1-Pentanol at 303.15 K. *J. Chem. Eng. Data* **1990**, *35*, 33−35.

TRC Thermodynamic Tables-Hydrocarbons; TRC, Texas A&M University: College Station, TX Oct 1977; p a1010.

TRC Thermodynamic Tables-Hydrocarbons; TRC, Texas A&M University: College Station, TX, 1992; p c1011.

Treszczanowicz, A. J.; Benson, G. C. Excess Volumes of Alkanol + n-Alkanes II. Binary Mixtures of n-Pentanol, n-Hexanol, n-Octanol, and n-Decanol + n-Heptane. *J. Chem. Thermodyn.* **1978**, *10*, 967−974.

Treszczanowicz, A. J.; Benson, G. C. Excess Volumes of Alkanol + n-Alkanes III. Binary Mixtures of Hexan-1-ol + n-Pentane, n-Hexane, n-Octane and n-Decane. *J. Chem. Thermodyn.* **1980**, *12*, 173−179.

Treszczanowicz, A. J.; Kiyohara, O.; Benson, G. C. Excess Volumes of Alkanol + n-Alkanes IV. Binary Mixtures of Decan-1-ol + n-Pentane, n-Hexane, n-Octane and n-Decane and n- Hexadecane. *J. Chem. Thermodyn.* **1981**, *13*, 253−260.

Treszczanowicz, A. J.; Treszczanowicz, T.; Benson, G. C. Review of Experimental and Recommended Data for the Excess Molar Volumes of 1-Alkanol + Alkane BInary mixtures. *Fluid Phase. Equilib.* **1993**, *89*, 31−56.

Vij, J. K.; Scaife, W. G.; Calderwood, J. H. The Pressure and Temperature Dependence of the Static Permittivity and Density of Heptanol Isomers. *J. Phys. D, Appl. Phys.* **1978**, *11*, 545−552.

Wagner, D.; Heintz, A. Excess Volumes of Binary 1-Alkanol/Nonane Mixtures at Temperatures between 293.15 and 333.15 K. *J. Chem. Eng. Data* **1986**, *31*, 483−487.

Zielkiewicz, J. Excess Volumes of (Heptane + Propane-2-ol, or Butan-1-ol or 2-Methyl Propan-1-ol or 2-Methyl Propane-2-ol or Pentan-1-ol at the Temperature 313.15 K. *J. Chem. Thermodyn.* **1994**, *26*, 959−964.

Received for review July 17, 1995. Revised manuscript received January 11, 1996. Accepted March 1, 1996.[⊗]

JE950172P

[⊗] Abstract published in *Advance ACS Abstracts*, April 15, 1996.