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Phase Equilibria and Volumetric Properties in Binary Mixtures Containing Branched Chain Ethers (Methyl 1,1-Dimethylethyl Ether or Ethyl 1,1-Dimethylethyl Ether or Methyl 1,1-Dimethylpropyl Ether or Ethyl 1,1-Dimethylpropyl Ether)

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The solid−liquid equilibrium (SLE) has been measured above 280 K for eight mixtures of *n*-alkanes (octadecane, eicosane, docosane, tetracosane, pentacosane, hexacosane, heptacosane, octacosane) with methyl 1,1-dimethylethyl ether (MTBE). Experimental results of solubility are compared with values calculated by means of the Wilson, UNIQUAC, and NRTL equations utilizing parameters taken from the SLE. The existence of a solid−solid first-order phase transition in hydrocarbons has been taken into consideration in the solubility calculations. The solubility of hydrocarbons in branched chain ethers is lower than that in *n*-alkanes but higher than that in cycloalkanes, branched alkanes, 1-alcohols, and *tert*-alcohols. The best correlation of the solubility data has been obtained by the NRTL equation, where the average root-mean-square deviation of the solubility temperatures is 0.46 K. The liquid−liquid equilibrium (LLE) has been measured between 300 and 360 K for binary mixtures of water with ethyl 1,1-dimethylethyl ether, methyl 1,1-dimethylpropyl ether, and ethyl 1,1-dimethylpropyl ether. The solubility of water in branched chain ether increases with increasing temperature, whereas the solubility of ether in water is decreasing up to 330 K and at the higher temperatures is slightly increasing. The excess molar volumes V_m^E have been measured at the temperatures 298.15 K and 308.15 K for binary mixtures of hexane, octane, decane, dodecane, tetradecane, hexadecane, cyclohexane, and 1-heptyne with ethyl 1,1-dimethylpropyl ether. The excess molar volumes of all mixtures except for 1-heptyne are positive over the whole composition range. The experimental results have been correlated with the Redlich−Kister polynomial and compared with the results predicted from Prigogine−Flory−Patterson theory. The interchange parameter X_{12}, which minimized V_m^E experimental data, was adjusted and then used to predict the heat of mixing.

Introduction

Tertiary ethers are important gasoline blending agents. The thermodynamic properties of mixtures containing methyl 1,1-dimethylethyl ether (MTBE) or ethyl 1,1-dimethylethyl ether (ETBE) or methyl 1,1-dimethylpropyl ether (MTAE) or ethyl 1,1-dimethylpropyl ether (ETAE) thus seemed to us to be an interesting topic to study. MTBE is the primary oxygenated compound being used to reformulate gasoline to improve its octane rating and pollution-reducing capability.

Many scientists (Ralston et al., 1944; Chang et al., 1983) measured the solubility of normal paraffins in various solvents. In the petroleum industry one of the main problems is to describe the solid−liquid equilibrium. The solid−liquid equilibrium (SLE) in mixtures formed by a *n*-paraffin and a hydrocarbon is discussed by many authors (Madsen and Boistelle, 1976; Dernini and De Santis, 1976; Domańska et al., 1987; Domańska and Kniaż, 1990; Książczak et al., 1994; Roberts et al., 1994). SLE diagrams for the *n*-paraffin with *n*-alkanol mixtures are of great importance to fat, cosmetic, and oil technology and research. Many authors (Plesnar et al., 1990; Domańska and Domański, 1991; Huyskens and Seghers, 1994) have published extensive solubility data. Solubilities of some normal paraffins (C_{18}−C_{28}) in *tert*-butyl alcohol have been measured by Domańska and González (1998) for improving the thermodynamic characterization of such mixtures in terms of the DISQUAC group contribution model. The solubility of *n*-alkanes in ETBE was measured by Domańska (1998), and that in ETAE will be published by Domańska and Morawski (1999). The purpose of this paper is to report the solubility of *n*-paraffin hydrocarbons (n = 18, 20, 22, 24, 25, 26, 27, 28) in MTBE.

Alkanols are used as well as fuel extenders for internal combustion engines. Unfortunately, the hygroscopic nature of alkanols can result in water being an important, albeit unwanted, component of motor fuel. For this reason we studied the liquid−liquid equilibrium (LLE) of (water + a branched ether) mixtures. The LLE in the binary system of water and MTBE in the temperature range from 273.15 K to 343.15 K was measured by Zikmundová et al. (1990). Ternary systems containing an alkanol (methanol, ethanol,

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Table 1. Physical Constants of Pure Compounds: T_m, Melting Point (this Work); ΔH_m, Molar Heat of Fusion; ΔH_{tr}, Molar Heat of Transition ($\alpha \rightarrow \beta$); ΔC_{p_m}, Heat Capacity Change at the Melting Temperature and $V^{273.15}$, Molar Volume and T_{tr}, Transition Temperature (this Work)

component	T_m/K	ΔH_m/(kJ mol^{-1})	ΔH_{tr}/(kJ mol^{-1})	ΔC_{p_m}/(J K mol^{-1})	V(273.15 K)^a/(cm^3 mol^{-1})	T_{tr}/K
octadecane	301.65	61.71^b		50.0^c	326.5	
eicosane	309.80	66.93^d	18.39^d	54.0^c	359.4	309.35
docosane	317.05	39.76^c	36.35^c	58.5^c	392.0	314.60
tetracosane	323.75	57.31^c	27.68^c	66.6^c	424.6	318.90
pentacosane	327.20	57.78^c	26.08^c	71.0^c	440.5	319.45
hexacosane	329.65	63.92^c	30.36^c	78.3^c	457.2	324.25
heptacosane	331.85	60.46^e	28.97^e	91.5^c	474.5	327.40
octacosane	334.60	66.52^c	33.60^c	118.9^c	489.8	330.80

[a] From Maffiolo et al., 1972. [b] From Van Oort and White, 1985. [c] From linear extrapolation of data for odd- (Messerly et al., 1967) and even-numbered *n*-alkanes from Domańska and Wyrzykowska-Stankiewicz, 1991. [d] From Claudy and Letoffe, 1991. [e] From Shaerer et al., 1955.

1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol) and MTBE and water at 298.15 K were measured by Letcher at al. (1991). The ternary liquid−liquid equilibrium data of (MTBE + water + 1-octanol) have been published as well by Aree et al. (1996) at two temperatures: 298.15 K and 308.15 K.

The purpose of this paper was to measure the liquid−liquid equilibrium in the binary system of water and ETBE or MTAE or ETAE in the temperature range from 300 K to 360 K.

Recent papers from our laboratory have reported measurements of excess molar volumes V_m^E of MTAE with *n*-alkanes (C_6−C_{16}) or benzene or cyclohexane at 298.15 K (Witek et al., 1997) and of excess volumes of hydrocarbons with MTBE or ETBE or MTAE at 298.15 K and 308.15 K (Domańska, 1997) and of excess molar enthalpies of hydrocarbons with MTBE or MTAE at 298.15 K and 308.15 K (Letcher and Domańska, 1997). The excess molar volumes V_m^E of ETAE with *n*-alkanes (C_6−C_{16}) or benzene or cyclohexane or 1-heptyne at 298.15 K and 308.15 K (Domańska and Łachwa, 1999) and the excess molar enthalpies H_m^E of hydrocarbons with ETAE at 298.15 K (Letcher and Domańska, 1999) have also been reported. The results were discussed in terms of the NRTL, UNIQUAC, and Prigogine−Flory−Patterson (PFP) models. Following this work we have determined V_m^E of mixtures formed by a hydrocarbon (hexane, octane, decane, dodecane, tetradecane, hexadecane, cyclohexane, 1-heptyne) and ETBE at 298.15 K and 308.15 K.

The excess molar heat capacities (C_p^E) and V_m^E of binary and quaternary mixtures of ETBE with hydrocarbons and ethanol were determined by Mier at al. (1994 and 1995), and those of mixture with alcohols (C_1−C_4) were determined by Oh and Park (1998).

The data presented here will be useful in the future for testing new theories of liquid mixtures using H_m^E, V_m^E, SLE, and LLE to predict the thermodynamic properties of mixtures containing branched chain ethers.

Experimental Section

The origins of the chemicals (in parentheses Chemical Abstracts registry numbers) and their mass percent purities are as follows: MTBE (methyl *tert*-butyl ether, 1634-04-4, Fluka AG, >98%), octadecane (593-45-3, Koch-Light Lab.), eicosane (112-95-8, Fluka AG), docosane (629-97-0, Fluka AG), tetracosane (646-31-1, Fluka AG), pentacosane (629-99-2, Fluka AG), hexacosane (630-01-3, INC Pharm), heptacosane (593-49-7, Fluka AG), octacosane (630-02-4, Fluka AG), hexane (110-54-3, Merck, >99%), octane (111-65-9, Aldrich, >99%), decane (124-18-5, Schuchardt, >99%), dodecane (112-40-3, BDH, >98%), tetradecane (629-59-4, Koch Light Lab., 98%), hexadecane (544-76-3, Int.E. L.W., >99.0%), cyclohexane (110-82-7, Int. E. L. W, 99.0%), 1-heptyne (628-71-7, Aldrich, 98%). ETBE (ethyl *tert*-butyl ether, 637-92-3) and ETAE (ethyl *tert*-amyl ether, 919-94-8) were synthesized at the Division of Organic Chemistry, Faculty of Chemistry, Warsaw University of Technology, Poland. MTBE and ATAE were fractionally distilled under pressure below atmospheric pressure after prolonged reflux over different drying reagents to a mass fraction purity better than 0.998 and 0.999. All liquids were stored over freshly activated molecular sieves of type 4A (Union Carbide). All compounds were checked by GLC analysis, and no significant impurities were found. Analysis, using the Karl-Fisher technique, showed that the impurity in each of the solvents was <0.02 mol %. Doubly redistilled water was used for LLE measurement and for the densitometer calibration. Commercially available *n*-alkanes were directly used without purification. The purity of octadecane was chromatographically determined to be 0.99. The purity of higher *n*-alkanes was 0.98. The physical properties of pure *n*-alkanes are collected in Table 1.

Solid−liquid equilibrium temperatures were determined using a dynamic method described in detail previously by Domańska (1986). Mixtures were heated very slowly (at <2 K h^{-1} near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell, placed in a thermostat. The crystal disappearance temperatures, detected visually, were measured with an Anschutz (TGL 11986, H. Schlegel, Ilmenau, Germany) thermometer (subdivided in 0.1 K) totally immersed in the thermostating liquid. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy of the temperature measurements was ±0.05 K. The error in the mole fraction did not exceed $\delta_{x_1} = 0.0005$.

Liquid−liquid equilibrium in binary systems (water + ETBE or MTAE or ETAE) was investigated in the temperature interval 300 K to 360 K by the following two methods: the direct synthetic method (in a water-rich phase) and the direct analytical method using a UV−vis spectrophotometer or Fisher method (in an ether-rich phase). The LLE temperature in a water rich phase was determined as an average of two temperatures during increasing and decreasing the temperature of two liquids' disappearance (the solution was no longer cloudy) or appearance, respectively. Mixtures were heated very slowly with continuous stirring inside a Pyrex glass, kept at constant temperature by circulated water. The equilibrium temperatures, detected visually, were measured with an Anschutz (TGL 11986, H. Schlegel, Ilmenau, Germany) thermometer (subdivided in 0.1 K) totally immersed in the thermostating liquid. The thermometer was calibrated on the basis of the ITS-90 scale of temperature. The accuracy

Table 2. Experimental Solid−Liquid Equilibrium Temperatures (T, Phases α and β, Respectively) for Hydrocarbon (1) + MTBE (2) Systems and the Experimental Activity Coefficient γ_1 of the Solute

x_1	T_α or T_β/K	γ_1	x_1	T_α or T_β/K	γ_1	x_1	T_α or T_β/K	γ_1	x_1	T_α or T_β/K	γ_1	x_1	T_α or T_β/K	γ_1
Octadecane														
0.0738	276.20 (α)	1.430	0.1749	283.85 (α)	1.234	0.3613	290.80 (α)	1.111	0.5714	295.45 (α)	1.047	0.7980	299.90 (α)	1.084
0.0830	277.35 (α)	1.419	0.1986	284.75 (α)	1.180	0.3847	291.35 (α)	1.093	0.6159	296.35 (α)	1.046	0.8571	300.75 (α)	1.084
0.0945	278.45 (α)	1.384	0.2279	286.10 (α)	1.158	0.4165	292.15 (α)	1.082	0.6529	297.15 (α)	1.054	0.9085	301.35 (α)	1.072
0.1087	279.45 (α)	1.323	0.2563	287.15 (α)	1.134	0.4547	293.05 (α)	1.070	0.6940	298.20 (α)	1.077	0.9501	301.45 (α)	1.035
0.1203	281.00 (α)	1.377	0.2827	288.30 (α)	1.137	0.4992	293.95 (α)	1.051	0.7245	298.80 (α)	1.092	1.0000	301.65 (α)	1.000
0.1483	282.20 (α)	1.249	0.3108	289.35 (α)	1.136	0.5329	294.70 (α)	1.050	0.7678	299.15 (α)	1.061			
Eicosane														
0.0856	286.60 (β)	0.825	0.2553	295.75 (β)	0.826	0.5068	302.45 (β)	0.893	0.7397	306.60 (β)	0.967	0.9229	308.80 (β)	0.983
0.1044	287.85 (β)	1.268	0.2776	296.65 (β)	0.843	0.5578	303.55 (β)	0.917	0.7615	306.90 (β)	0.970	0.9376	309.00 (β)	0.989
0.1247	289.65 (β)	1.218	0.3267	298.10 (β)	0.846	0.5990	304.30 (β)	0.928	0.7843	307.20 (β)	0.973	0.9557	309.15 (β)	0.986
0.1398	290.70 (β)	0.831	0.3569	298.80 (β)	0.840	0.6264	304.80 (β)	0.938	0.8015	307.45 (β)	0.979	0.9756	309.35 (β)	0.987
0.1642	291.95 (β)	0.822	0.3634	299.00 (β)	0.844	0.6572	305.30 (β)	0.944	0.8627	308.10 (β)	0.976	0.9872	309.45 (α)	0.984
0.1811	292.70 (β)	0.814	0.4092	300.25 (β)	0.864	0.6843	305.70 (β)	0.947	0.8854	308.35 (β)	0.977	0.9917	309.80 (α)	0.987
0.2252	294.50 (β)	0.809	0.4603	301.40 (β)	0.874	0.7130	306.20 (β)	0.960	0.9020	308.55 (β)	0.979	1.0000	309.80 (α)	1.000
Docosane														
0.0311	286.50 (β)	1.710	0.1299	297.95 (β)	1.365	0.3841	307.60 (β)	1.198	0.6227	312.15 (β)	1.137	0.8254	314.60 (α)	1.078
0.0364	287.75 (β)	1.673	0.1441	298.80 (β)	1.342	0.4200	308.45 (β)	1.188	0.6577	312.65 (β)	1.128	0.8402	315.15 (α)	1.087
0.0439	289.20 (β)	1.622	0.1748	300.50 (β)	1.312	0.4432	308.95 (β)	1.181	0.6711	312.90 (β)	1.132	0.8587	315.65 (α)	1.089
0.0537	290.75 (β)	1.564	0.2039	301.80 (β)	1.281	0.4818	309.65 (β)	1.161	0.7055	313.40 (β)	1.128	0.8831	315.95 (α)	1.075
0.0692	292.90 (β)	1.522	0.2287	302.90 (β)	1.273	0.5031	310.15 (β)	1.166	0.7242	313.70 (β)	1.130	0.9101	316.20 (α)	1.055
0.0858	294.50 (β)	1.451	0.2511	303.70 (β)	1.255	0.5275	310.65 (β)	1.166	0.7479	313.90 (β)	1.115	0.9189	316.35 (α)	1.053
0.0995	295.75 (β)	1.423	0.2952	304.85 (β)	1.194	0.5560	311.05 (β)	1.149	0.7711	314.20 (β)	1.112	0.9452	316.65 (α)	1.038
0.1085	296.50 (β)	1.410	0.3528	306.65 (β)	1.190	0.5928	311.75 (β)	1.151	0.8062	314.35 (β)	1.078	1.0000	317.05 (α)	1.000
Tetracosane														
0.0606	298.10 (β)	1.311	0.2245	308.85 (β)	1.146	0.4966	316.55 (β)	1.150	0.6601	318.75 (β)	1.081	0.8464	321.80 (α)	1.039
0.0769	300.40 (β)	1.337	0.2737	310.40 (β)	1.107	0.5242	317.05 (β)	1.147	0.6805	318.85 (β)	1.059	0.8557	322.00 (α)	1.041
0.1100	302.65 (β)	1.198	0.3271	312.15 (β)	1.112	0.5432	317.40 (β)	1.146	0.7329	319.75 (α)	1.046	0.8904	322.50 (α)	1.034
0.1353	304.55 (β)	1.199	0.3627	313.20 (β)	1.118	0.5659	317.75 (β)	1.140	0.7542	320.25 (α)	1.051	0.9138	322.85 (α)	1.031
0.1590	305.70 (β)	1.155	0.4002	314.20 (β)	1.123	0.5927	318.15 (β)	1.133	0.7674	320.45 (α)	1.047	0.9593	323.40 (α)	1.019
0.1860	307.10 (β)	1.148	0.4361	315.15 (β)	1.136	0.6163	318.45 (β)	1.123	0.7780	320.65 (α)	1.047	1.0000	323.75 (α)	1.000
0.2106	308.25 (β)	1.146	0.4701	315.95 (β)	1.144	0.6406	318.65 (β)	1.102	0.8165	321.35 (α)	1.045			
Pentacosane														
0.0416	297.90 (β)	1.521	0.2499	310.85 (β)	1.009	0.5472	318.75 (β)	1.022	0.7569	323.20 (α)	1.016	0.9399	326.05 (α)	0.987
0.0614	301.00 (β)	1.448	0.2886	312.35 (β)	1.019	0.5776	319.15 (β)	1.007	0.7950	323.90 (α)	1.014	0.9651	326.55 (α)	0.993
0.0739	302.55 (β)	1.423	0.3415	313.90 (β)	1.008	0.6098	319.85 (α)	1.009	0.8480	324.75 (α)	1.005	1.0000	327.20 (α)	1.000
0.1061	304.45 (β)	1.216	0.4002	315.60 (β)	1.021	0.6353	320.80 (α)	1.032	0.8734	325.15 (α)	1.002			
0.1251	305.70 (β)	1.178	0.4492	316.85 (β)	1.031	0.6716	321.70 (α)	1.037	0.8844	325.40 (α)	1.006			
0.1572	307.35 (β)	1.115	0.4996	317.90 (β)	1.029	0.6939	322.15 (α)	1.034	0.8972	325.55 (α)	1.001			
0.2006	309.00 (β)	1.038	0.5259	318.40 (β)	1.027	0.7249	322.70 (α)	1.027	0.9166	325.75 (α)	0.993			
Hexacosane														
0.0654	304.65 (β)	1.142	0.4105	320.25 (β)	1.072	0.6196	324.25 (α)	1.096	0.7816	327.50 (α)	1.098	0.9100	328.95 (α)	1.046
0.1005	307.95 (β)	1.084	0.4399	321.00 (β)	1.086	0.6363	324.75 (α)	1.107	0.7946	327.70 (α)	1.096	0.9277	329.05 (α)	1.033
0.1392	310.60 (β)	1.066	0.4880	322.05 (β)	1.097	0.6556	325.30 (α)	1.118	0.8161	327.95 (α)	1.086	0.9584	329.40 (α)	1.025
0.1770	312.30 (β)	1.019	0.5290	322.90 (β)	1.110	0.6827	325.95 (α)	1.125	0.8284	328.10 (α)	1.081	1.0000	329.65 (α)	1.000
0.2134	313.85 (β)	1.009	0.5552	323.40 (β)	1.116	0.7094	326.35 (α)	1.114	0.8494	328.35 (α)	1.074			
0.2503	315.35 (β)	1.019	0.5710	323.65 (β)	1.115	0.7343	326.85 (α)	1.116	0.8651	328.55 (α)	1.069			
0.2944	317.05 (β)	1.049	0.5804	323.75 (β)	1.108	0.7481	327.05 (α)	1.111	0.8776	328.70 (α)	1.065			
0.3516	318.70 (β)	1.055	0.5983	324.00 (β)	1.105	0.7670	327.30 (α)	1.103	0.8885	328.75 (α)	1.056			
Heptacosane														
0.0477	304.90 (β)	1.435	0.2934	319.15 (β)	1.092	0.4988	324.90 (β)	1.159	0.6989	329.50 (α)	1.224	0.8689	331.00 (α)	1.088
0.0811	308.35 (β)	1.240	0.3181	320.00 (β)	1.100	0.5480	326.05 (β)	1.185	0.7243	329.80 (α)	1.205	0.9078	331.20 (α)	1.055
0.1233	311.65 (β)	1.170	0.3475	320.80 (β)	1.094	0.5775	326.70 (β)	1.200	0.7687	330.20 (α)	1.166	0.9251	331.35 (α)	1.046
0.1569	313.70 (β)	1.147	0.3762	321.65 (β)	1.103	0.6052	327.40 (α)	1.228	0.7895	330.40 (α)	1.151	0.9537	331.50 (α)	1.025
0.2051	315.85 (β)	1.104	0.4150	322.70 (β)	1.114	0.6363	328.55 (α)	1.262	0.8101	330.60 (α)	1.136	1.0000	331.85 (α)	1.000
0.2502	317.65 (β)	1.094	0.4526	323.70 (β)	1.131	0.6754	329.15 (α)	1.238	0.8507	330.85 (α)	1.100			
Octacosane														
0.0266	304.85 (β)	1.371	0.2469	320.75 (β)	0.996	0.5732	329.05 (β)	1.094	0.7059	330.80 (α)	1.077	0.8526	333.65 (α)	1.096
0.0464	308.45 (β)	1.228	0.2872	322.45 (β)	1.040	0.5938	329.35 (β)	1.092	0.7199	331.25 (α)	1.092	0.8675	333.80 (α)	1.089
0.0699	310.80 (β)	1.086	0.3301	323.85 (β)	1.061	0.6110	329.65 (β)	1.097	0.7334	331.65 (α)	1.103	0.9067	333.90 (α)	1.049
0.0929	313.30 (β)	1.104	0.3914	325.40 (β)	1.067	0.6418	330.15 (β)	1.103	0.7585	332.25 (α)	1.114	0.9269	334.25 (α)	1.052
0.1440	316.15 (β)	0.999	0.4569	326.85 (β)	1.075	0.6553	330.30 (β)	1.099	0.7784	332.55 (α)	1.109	0.9531	334.35 (α)	1.031
0.1723	317.45 (β)	0.973	0.5019	327.70 (β)	1.076	0.6751	330.50 (β)	1.090	0.8032	333.00 (α)	1.111	1.0000	334.60 (α)	1.000
0.2040	319.10 (β)	0.996	0.5400	328.45 (β)	1.087	0.6843	330.65 (β)	1.093	0.8312	333.40 (α)	1.104			

of temperature measurements was ±0.05 K. The error in the mole fraction did not exceed $\delta_{x_1} = 0.0005$, measured as for the SLE (Domańska, 1986). The accuracy of the temperature measurements was ±0.05 K. Mixtures were prepared by weighing. In the ether-rich phase LLE measurements were carried out for 3 h in the same ampule (30 cm^3) with a magnetic stirrer. A sample for the analysis was taken with a syringe. The water content in the ether phase was determined with a Karl-Fisher apparatus (Aqualometer AQ 861, Apel) or with a UV−vis CARY 2315 Varian spectrophotometer (λ = 192 nm) according to the calibration curve.

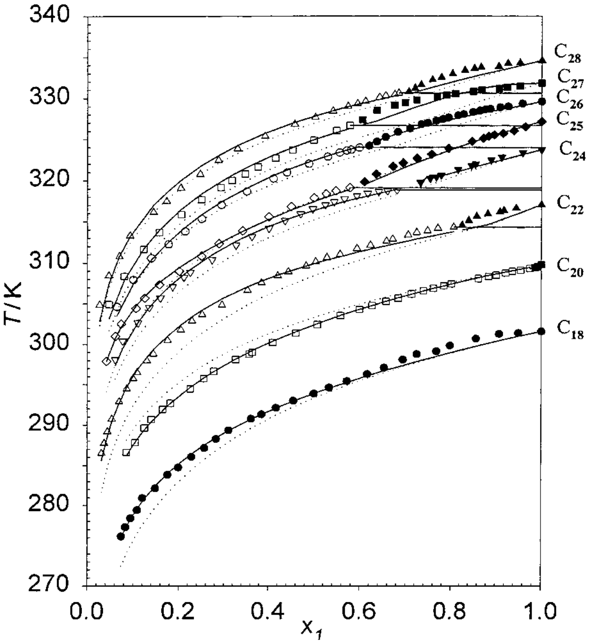

Figure 1. Solubility of a hydrocarbon (1) in MTBE (2). Experimental data: solid points, phase α; hollow points, phase β; solid lines, calculated by the NRTL equation; doted lines, ideal solubility.

An Anton Paar DMA 602 vibrating-tube densitometer thermostated at $T = (298.15 \pm 0.01)$ K or (308.15 ± 0.01) K was used to determine the V_m^E values. The densitometer's calibration was performed at atmospheric pressure using doubly distilled and degassed water, special purified benzene (CHEMIPAN, Poland, 0.999), and dried air. The vibrating-tube temperature was measured with an Anton Paar DM 100-30 digital thermometer and was regulated to within better than ±0.01 K using a UNIPAN 60 thermostat and a 202 temperature control system (UNIPAN, Poland). Mixtures were prepared by weighing, the error in mole fraction being estimated as less than 5×10^{-5}.

Results and Discussion

1. Solid−Liquid Equilibria of n-Alkanes in Methyl 1,1-Dimethylethyl Ether. Table 2 list the direct experimental results of the SLE temperatures T versus x_1, the mole fraction of the n-alkanes of two crystallographic forms α and β, for the investigated systems. The experimental values of the temperature (T_{tr}) at which the solid−solid phase transition occurs (all of them determined graphically) are collected in Table 1, and they are very close to the pure compound transition temperatures measured by Shaerr et al. (1955). Experimental phase diagrams of SLE investigated in this work are characterized mainly by the following: (i) positive deviations from ideality were found; thus, the solubility is lower than the ideal one, $\gamma_1 > 0$, for all systems, except the one with eicosane (see the values of the activity coefficients in Table 2 and Figure 1); (ii) the solubility of n-paraffins in MTBE decreases with increasing number of carbon atoms; (iii) the liquidus curves of the odd-numbered n-alkanes exhibit different shapes compared with those for the even-numbered n-alkanes (see Figure 1).

The solubility of a solid 1 in a liquid may be expressed in a very general manner by eq 1

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) - \frac{\Delta C_{p_{m1}}}{R}\left(\ln\frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \ln \gamma_1 \quad (1)$$

where x_1, γ_1, ΔH_{m1}, $\Delta C_{p_{m1}}$, T_{m1}, and T stand for the mole fraction, the activity coefficient, the enthalpy of fusion, the difference in the solute heat capacity between the solid and the liquid at the melting point, the melting point of the solute, and the equilibrium temperature, respectively. If the solid−solid transition occurs before fusion, an additional term must be added to the right-hand side of eq 1 (Weimar and Prausnitz, 1965; Choi and Mc Laughlin, 1983).

The solubility equation for temperatures below that of the phase transition must include the effect of the transition. The result for the first-order transition is

$$-\ln x_1 = \frac{\Delta H_{m1}}{R}\left(\frac{1}{T} - \frac{1}{T_{m1}}\right) - \frac{\Delta C_{p_{m1}}}{R}\left(\ln\frac{T}{T_{m1}} + \frac{T_{m1}}{T} - 1\right) + \frac{\Delta H'_{tr1}}{R}\left(\frac{1}{T} - \frac{1}{T'_{tr1}}\right) + \ln \gamma_1 \quad (2)$$

where $\Delta H'_{tr1}$ and T'_{tr1} stand for the enthalpy of transition and the transition temperature of the solute, respectively.

Table 3. Correlation of the Solubility Data, SLE, of a Hydrocarbon (1) + MTBE (2) Mixture by Means of the Wilson, UNIQUAC, and NRTL Equations: Values of Parameters and Measures of Deviations

	parameter			σ_T[b]/K		
hydrocarbon	Wilson $g_{12} - g_{22}$/(J mol^{-1}) $g_{21} - g_{11}$/(J mol^{-1})	UNIQUAC Δu_{12}/(J mol^{-1}) Δu_{21}/(J mol^{-1})	NRTL[a] Δg_{12}/(J mol^{-1}) Δg_{21}/(J mol^{-1})	Wilson	UNIQUAC	NRTL
octadecane	−426.82 1589.89	919.15 −425.28	−342.99 1433.29	0.45	0.45	0.45
eicosane	3924.96 −223.83	−1161.28 1822.97	971.00 −1316.16	0.22	0.22	0.15
docosane	−2664.48 4021.46	1698.22 −835.04	1196.62 317.32	0.67	0.77	0.64
tetracosane	−4352.13 5973.33	1898.29 −999.34	2073.57 −536.19	0.38	0.56	0.35
pentacosane	1307.30 1305.56	519.35 −14.50	−1101.53 3111.55	0.31	0.32	0.32
hexacosane	−5887.87 10731.40	2004.26 −1092.57	4062.53 −1097.19	0.36	0.87	0.36
heptacosane	−5715.10 11453.90	1906.74 −968.22	10045.95 95.30	0.83	1.42	0.67
octacosane	−5272.14 6925.74	1202.22 −559.19	2600.42 −915.44	0.78	0.89	0.72

[a] Calculated with the third nonrandomness parameter α = 0.85. [b] According to eq 4 in the text.

Table 4. Experimental Liquid−Liquid Equilibrium Temperatures for Water (1) + ETBE or MTAE or ETAE (2) Systems

ether rich		water rich	
10^2x_1	T/K	10^2x_1	T/K
	ETBE		
4.09	279.05	99.86	283.15
4.68	288.75	99.88	290.65
5.31	298.15	99.90	300.65
5.55[a]	298.15	99.90	308.25
5.88	303.15	99.91	315.75
6.09[a]	303.15	99.91	325.65
6.29	308.15	99.91	329.95
6.52[a]	308.15	99.90	330.20
6.70	310.15	99.89	340.35
6.97	313.15	99.87	342.30
7.22[a]	313.15	99.86	347.45
7.83	318.15	99.85	353.05
9.69	328.15	99.84	356.60
11.62	338.15	99.83	361.55
13.70	348.15	99.83	364.45
		99.82	364.65
	MTAE		
1.30	278.15	99.78	282.45
1.42	283.15	99.80	290.65
1.79	288.15	99.83	297.40
2.15	293.15	99.85	304.65
2.60[a]	298.15	99.87	313.15
2.63	298.15	99.88	323.15
2.88[a]	303.15	99.88	332.30
2.90	303.15	99.88	344.35
3.81	308.15	99.87	352.50
4.12	313.15	99.87	357.75
4.21[a]	313.15	99.86	362.65
4.95	318.15		
6.65	328.15		
8.38	338.15		
10.35	348.15		
	ETAE		
0.237	283.15	99.90	289.40
0.248	292.75	99.91	297.95
0.251	294.85	99.91	307.25
0.270	305.45	99.92	318.15
0.291	315.25	99.92	329.15
0.323	328.15	99.92	341.65
0.352	338.15	99.92	351.65
		99.92	363.65

[a] Fisher method.

In this study three methods are used to derive the solute activity coefficients γ_1 from the so-called correlation equations that describe the Gibbs excess free energy of mixing G^E, the Wilson (Wilson, 1964), UNIQUAC (Abrams and Prausnitz, 1975), and NRTL (Renon and Prausnitz, 1968) methods. The exact mathematical forms of the equations have been presented in our previous paper (Domańska, 1989a). The parameter α_{12}, a constant of proportionality similar to the nonrandomness constant of the NRTL equation, was $\alpha_{12} = \alpha_{21} = 0.85$.

The parameters of the equations were found by an optimization technique using Marquardt's maximum neighborhood method of minimization (Marquardt, 1963):

$$\Omega = \sum_{i=1}^{n} [T_i^{\text{exp}} - T_i^{\text{cal}}(x_{1i},P_1,P_2)]^2 \qquad (3)$$

where Ω is the objective function, T_i^{exp} denotes an experimental value of the temperature for a given concentration x_{1i}, and T_i^{cal} is the temperature calculated for a given concentration x_{1i} and parameters P_1 and P_2, obtained by solving the nonlinear equation (eq 1 or 2), depending upon the value of temperature and the expression for the logarithm of the activity according to the assumed model. The nonlinear equations were solved using the secant method. The root-mean-square deviation of temperature (σ_T defined by eq 4) was used as a measure of the goodness of the solubility correlation.

$$\sigma_T = \left(\sum_{i=1}^{n} \frac{(T_i^{\text{cal}} - T_i)^2}{n - 2} \right)^{1/2} \qquad (4)$$

where T_i^{exp} and T_i^{cal} are, respectively, the experimental and calculated temperatures of the i-th point, n is the number of experimental points (including the melting point), and 2 is the number of adjustable parameters.

Table 3 lists the results of fitting the solubility curves by the three equations used: Wilson, UNIQUAC, and NRTL. The UNIQUAC structural parameters for the pure components were obtained from

$$r_i = 0.029281 V_m \qquad (5)$$

$$q_i = \frac{(Z - 2)r_i}{Z} + \frac{2(1 - l_i)}{Z} \qquad (6)$$

where V_m is the molar volume of pure component i at 298.15 K, Z is the coordination number, assumed to be equal to 10, and l_i is the bulk factor; it was assumed that $l_i = 0$.

For the eight systems presented in this work the best description of the solid−liquid equilibrium was given by

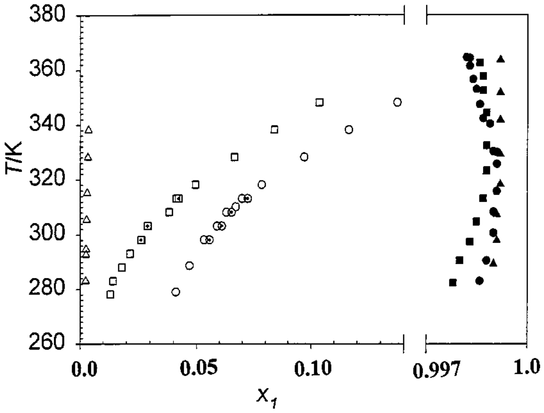

Figure 2. Temperature dependence of the mutual solubility in the systems: ●, water (1) + ETBE (2); ■, water (1) + MTAE (2); △, water (1) + ETAE (2); solid points, water reach phase; hollow points, ether reach phase; crosses, points obtained by the Fisher method.

Table 5. Densities of Pure Substances ρ at 298.15 K and 308.15 K

	ρ/(kg dm^{-3})		
component	measured (298.15 K)	ref (298.15 K)	measured (308.15 K)
ETBE	0.735 57	0.735 28[a]	0.727 81
hexane	0.654 79	0.655 04[b]	0.647 40
octane	0.698 50	0.698 73[b]	0.692 71
decane	0.726 30	0.726 28[b]	0.721 09
dodecane	0.745 17	0.745 31[b]	0.740 33
tetradecane	0.759 35	0.759 29[b]	0.755 26
hexadecane	0.769 99	0.770 06[b]	0.765 31
cyclohexane	0.773 98	0.773 89[c]	0.767 13
1-heptyne	0.728 33	0.727 90[c]	0.721 62

[a] Domańska (1997). [b] Zhu et al. (1994a). [c] Riddick et al. (1986).

Table 6. Experimental Excess Molar Volumes V_m^E for Binary Mixtures of x_1Hydrocarbon + $(1 - x_1)$ETBE and Deviations δV_m^E at the Temperature 298.15 K

x_1	V_m^E/ $(cm^3\ mol^{-1})$	$10^3\delta V_m^E$/ $(cm^3\ mol^{-1})$	x_1	V_m^E/ $(cm^3\ mol^{-1})$	$10^3\delta V_m^E$/ $(cm^3\ mol^{-1})$	x_1	V_m^E/ $(cm^3\ mol^{-1})$	$10^3\delta V_m^E$/ $(cm^3\ mol^{-1})$	x_1	V_m^E/ $(cm^3\ mol^{-1})$	$10^3\delta V_m^E$/ $(cm^3\ mol^{-1})$
x_1Hexane + $(1 - x_1)$ETBE											
0.0055	0.0103	5.5	0.2140	0.1460	−3.0	0.5014	0.2293	4.6	0.8299	0.1342	5.2
0.0214	0.0248	6.4	0.2424	0.1609	−2.0	0.5636	0.2217	0.0	0.8497	0.1145	−2.2
0.0461	0.0369	−1.7	0.3768	0.2069	−2.9	0.6454	0.2048	−2.4	0.9184	0.0741	5.3
0.1236	0.0944	−1.1	0.3860	0.2149	3.1	0.7118	0.1821	−4.3	0.9993	0.0081	7.4
0.1812	0.1365	5.3	0.4625	0.2218	−1.3	0.7889	0.1507	−1.1	0.9999	0.0020	1.9
x_1Octane + $(1 - x_1)$ETBE											
0.0197	0.0088	−16.8	0.2722	0.2556	−3.3	0.4276	0.3270	3.6	0.7858	0.2316	−7.7
0.0334	0.0406	−2.0	0.3378	0.2919	−1.3	0.4599	0.3328	3.3	0.8547	0.1812	1.0
0.0656	0.0766	−4.0	0.3454	0.2965	0.0	0.5093	0.3391	5.2	0.9401	0.1057	21.7
0.0688	0.0805	−3.7	0.3574	0.2989	−2.5	0.6009	0.3253	−0.4	0.9870	0.0291	9.6
0.1603	0.1828	6.9	0.3896	0.3171	4.1	0.6633	0.2959	−11.6	0.9965	0.0073	2.0
x_1Decane + $(1 - x_1)$ETBE											
0.0155	0.0161	2.5	0.1929	0.1407	−0.9	0.4152	0.2226	−2.9	0.8026	0.1508	−1.8
0.0383	0.0382	5.3	0.2629	0.1768	−0.6	0.4687	0.2323	−0.1	0.8644	0.1160	2.5
0.0605	0.0574	6.4	0.3286	0.1994	−3.8	0.5120	0.2382	4.0	0.9280	0.0763	11.2
0.0697	0.0606	2.4	0.3578	0.2110	−1.3	0.5760	0.2319	1.5	0.9823	0.0222	5.2
0.1311	0.1077	4.7	0.3899	0.2202	−0.3	0.6706	0.2042	−6.0	0.9972	0.0086	5.9
x_1Dodecane + $(1 - x_1)$ETBE											
0.0066	0.0021	−0.2	0.2600	0.0955	2.4	0.4154	0.1478	−5.1	0.8119	0.0987	−2.3
0.0482	0.0136	−1.7	0.2875	0.1054	−0.1	0.4260	0.1564	0.9	0.9336	0.0560	3.2
0.0565	0.0199	2.2	0.3440	0.1297	0.4	0.4745	0.1675	3.5	0.9551	0.0406	1.3
0.1141	0.0319	−3.0	0.3653	0.1367	−0.6	0.5350	0.1672	0.7	0.9599	0.0346	−1.3
0.1826	0.0617	2.1	0.3818	0.1410	−1.9	0.6235	0.1558	0.7	0.9871	0.0092	−4.0
x_1Tetradecane + $(1 - x_1)$ETBE											
0.0026	0.0064	6.1	0.2181	0.0603	−10.3	0.3418	0.1151	2.5	0.6029	0.1252	−6.9
0.0030	0.0079	7.5	0.2920	0.0916	−5.8	0.3602	0.1237	6.3	0.8237	0.0679	−4.3
0.0272	0.0115	6.7	0.3142	0.1014	−3.1	0.3899	0.1324	8.2	0.9015	0.0434	2.3
0.0842	0.0279	7.5	0.3159	0.1003	−4.8	0.4299	0.1338	2.6	0.9817	0.0196	12.0
0.1616	0.0506	1.9	0.3343	0.1083	−2.2	0.5051	0.1427	5.1	0.9926	0.0108	7.7
x_1Hexadecane + $(1 - x_1)$ETBE											
0.0194	0.0034	−3.1	0.1976	0.0673	1.6	0.3260	0.1006	0.9	0.5962	0.1142	−6.9
0.0339	0.0133	1.8	0.2495	0.0784	−2.4	0.3642	0.1121	4.9	0.7427	0.0904	−7.3
0.0382	0.0135	0.6	0.2860	0.0879	−2.5	0.3714	0.1117	3.1	0.8959	0.0507	3.6
0.0695	0.0235	−0.1	0.2881	0.0864	−4.5	0.4120	0.1184	3.5	0.9663	0.0289	12.7
0.1468	0.0454	−4.1	0.3247	0.1005	1.2	0.4934	0.1268	4.5	0.9775	0.0174	6.5
x_1Cyclohexane + $(1 - x_1)$ETBE											
0.0026	0.0064	4.9	0.2245	0.1173	−3.9	0.5014	0.1901	4.0	0.8544	0.0878	4.3
0.0183	0.0109	0.1	0.2553	0.1291	−5.1	0.6225	0.1716	−1.4	0.9153	0.0563	6.4
0.0335	0.0183	−1.4	0.3381	0.1619	−0.8	0.7332	0.1374	−2.1	0.9332	0.0244	−15.2
0.1514	0.0892	3.4	0.3746	0.1733	1.4	0.7841	0.1196	1.4	0.9868	0.0119	4.0
0.1721	0.1016	5.2	0.4512	0.1826	−1.3	0.8314	0.0957	0.2	0.9992	0.0037	3.2
$x_1$1-Heptyne + $(1 - x_1)$ETBE											
0.0232	−0.0402	0.3	0.4496	−0.3402	−1.3	0.6751	−0.3180	3.7	0.9213	−0.1455	3.6
0.0611	−0.1121	−12.2	0.4751	−0.3441	−3.8	0.7513	−0.2881	8.4	0.9533	−0.1010	−3.9
0.1251	−0.1781	3.4	0.5088	−0.3457	−5.0	0.8132	−0.2586	3.2	0.9751	−0.0566	−1.5
0.2232	−0.2641	2.9	0.5514	−0.3421	−2.9	0.8745	−0.2274	−19.2	0.9913	−0.0204	−0.3
0.3156	−0.3064	6.3	0.6512	−0.3264	0.5	0.8913	−0.1813	7.8	0.9933	−0.0133	2.3

the two-parameter NRTL equation with the average standard deviation $\sigma_T = 0.46$ K. For the two other equations, the standard deviations were slightly worse: $\sigma_T = 0.50$ K and $\sigma_T = 0.69$ K for the Wilson and UNIQUAC equations, respectively.

In our previous work, it was noted that the solubility of *n*-alkanes was lower in 1-alcohols than in *n*-alkanes and cycloalkanes (Domańska et al., 1987; Domańska, 1989b). The solubility of hydrocarbons in *tert*-butyl alcohol is higher than that in 1-alcohols (Domańska and González, 1998). The results of solid−liquid equilibrium measurements, presented in this paper, show worse solubility in MTBE than in heptane but even better solubility than that in cyclohexane and branched alkanes and much better solubility than that in 1-alcohols.

2. Liquid−Liquid Equilibria for (Water + Ethyl 1,1-Dimethylethyl Ether or Methyl 1,1-Dimethylpropyl Ether or Ethyl 1,1-Dimethylpropyl Ether). Table 4 lists the equilibrium compositions of the aqueous and ether phases at the temperature range from 300 K to 360 K for ETBE, MTAE, and ETAE. Temperature had almost no influence on the immiscible region. The solubilities of the partially miscible binaries at $T = 298.15$ K, expressed as mole ratios, are 0.0011 for ETBE in H_2O, 0.0531 for H_2O in ETBE, 0.0016 for MTAE in H_2O, 0.0260 for H_2O in MTAE, 0.0009 for ETAE in H_2O, and 0.0025 for nH_2O in ETAE. In addition to the almost total insolubility of these two compounds in each other at the temperatures under consideration, it can be noted that mutual solubility decreases in the order ETBE > MTAE > ETAE. Results are presented in Figure 2.

The data obtained are in good agreement with those of Zikmundová et al. (1990) for the system (water + MTBE). The manner of the temperature dependence (see Figure 2) implies that the solubility of water in a branched chain ether is increasing with rising temperature, whereas the

Table 7. Experimental Excess Molar Volumes $V_{\mathrm{m}}^{\mathrm{E}}$ for Binary Mixtures of x_1Hydrocarbon + $(1 - x_1)$ETBE and Deviations $\delta V_{\mathrm{m}}^{\mathrm{E}}$ at the Temperature 308.15 K

x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$10^3\delta V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$10^3\delta V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$10^3\delta V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	x_1	$V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)	$10^3\delta V_{\mathrm{m}}^{\mathrm{E}}$ ($\mathrm{cm^3\,mol^{-1}}$)
x_1 Hexane + $(1 - x_1)$ ETBE											
0.0037	0.0126	9.1	0.4173	0.2405	−0.9	0.5335	0.2476	−0.6	0.6902	0.2080	−6.8
0.0461	0.0564	13.4	0.4521	0.2454	−0.8	0.5553	0.2475	0.9	0.7764	0.1745	−0.5
0.1596	0.1373	5.7	0.4665	0.2443	−3.3	0.5675	0.2468	1.6	0.8915	0.1105	12.5
0.2877	0.2021	−0.2	0.4757	0.2496	1.4	0.5829	0.2405	−2.6	0.9568	0.0603	18.3
0.3447	0.2220	−1.5	0.5129	0.2505	1.5	0.6223	0.2321	−3.3	0.9955	0.0156	11.0
x_1 Octane + $(1 - x_1)$ ETBE											
0.0112	0.0114	−12.1	0.3885	0.3565	−2.1	0.4763	0.3717	3.4	0.6422	0.3486	−1.9
0.0344	0.0662	−2.1	0.4008	0.3603	−0.5	0.5040	0.3729	4.2	0.7311	0.3127	−3.9
0.1271	0.2127	7.5	0.4126	0.3614	−1.3	0.5337	0.3684	0.8	0.8314	0.2459	−0.2
0.2324	0.2945	−3.2	0.4296	0.3629	−1.9	0.5357	0.3672	−0.3	0.9027	0.1712	5.1
0.3130	0.3360	−1.7	0.4737	0.3702	2.0	0.5941	0.3611	0.3	0.9874	0.0176	−8.3
x_1 Decane + $(1 - x_1)$ ETBE											
0.0001	0.0105	10.4	0.3133	0.2264	−3.3	0.4389	0.2553	0.3	0.6203	0.2463	4.5
0.0282	0.0330	−0.7	0.3300	0.2306	−4.2	0.4440	0.2565	1.1	0.7030	0.1991	−17.4
0.1004	0.1133	7.0	0.3775	0.2464	0.1	0.4569	0.2600	3.8	0.8239	0.1602	5.6
0.2119	0.1846	−0.8	0.3823	0.2467	−0.5	0.5009	0.2614	4.6	0.9219	0.0828	3.6
0.2845	0.2159	−3.5	0.4130	0.2518	−0.3	0.5356	0.2594	4.4	0.9999	0.0203	20.2
x_1 Dodecane + $(1 - x_1)$ ETBE											
0.0107	0.0069	−2.4	0.2920	0.1412	4.5	0.3978	0.1752	−2.3	0.6266	0.1803	−3.6
0.0389	0.0197	−9.8	0.3497	0.1558	−4.6	0.4171	0.1821	−1.0	0.6935	0.1607	−1.6
0.1015	0.0604	0.3	0.3584	0.1589	−4.8	0.4310	0.1856	−1.1	0.8485	0.0952	−2.6
0.1750	0.0976	9.2	0.3773	0.1719	1.3	0.4782	0.1987	3.2	0.9002	0.0752	2.1
0.2788	0.1276	−3.3	0.3945	0.1751	−1.3	0.5387	0.2078	10.0	0.9818	0.0224	4.3
x_1 Tetradecane + $(1 - x_1)$ ETBE											
0.0093	0.0103	5.8	0.2391	0.0927	−0.2	0.3446	0.1342	1.0	0.5692	0.1541	−1.5
0.0361	0.0163	0.3	0.2728	0.1060	−0.6	0.3955	0.1485	0.8	0.7474	0.1142	0.5
0.0369	0.0172	0.8	0.3076	0.1208	0.7	0.4394	0.1565	0.5	0.8223	0.0946	1.5
0.0568	0.0224	−1.5	0.3227	0.1272	1.6	0.4715	0.1586	−0.9	0.9125	0.0598	−3.1
0.1659	0.0630	−0.6	0.3376	0.1286	−2.2	0.5243	0.1605	0.6	0.9741	0.0282	3.1
x Hexadecane + $(1 - x_1)$ ETBE											
0.0029	0.0124	10.9	0.1435	0.0614	−4.7	0.3234	0.1176	0.8	0.7287	0.0921	−14.9
0.0042	0.0130	10.8	0.1957	0.0753	−9.2	0.4291	0.1361	6.1	0.8700	0.0646	0.6
0.0218	0.0252	13.8	0.2810	0.1040	−4.0	0.4655	0.1371	5.3	0.8870	0.0605	3.3
0.0439	0.0328	10.3	0.2914	0.1103	−0.1	0.5543	0.1367	5.7	0.8915	0.0586	3.3
0.0562	0.0345	6.0	0.3129	0.1124	−2.4	0.6628	0.1186	−1.0	0.9529	0.0330	6.6
x_1 Cyclohexane + $(1 - x_1)$ ETBE											
0.0150	0.0160	3.5	0.2726	0.1693	−1.1	0.6158	0.2022	−4.9	0.8760	0.0923	−4.1
0.0307	0.0341	8.9	0.3753	0.2092	6.7	0.6955	0.1813	−4.8	0.9258	0.0682	7.0
0.0651	0.0511	−0.6	0.4559	0.2128	−2.4	0.7512	0.1694	4.6	0.9506	0.0468	5.0
0.1318	0.1081	10.6	0.5164	0.2200	2.6	0.8067	0.1361	−1.8	0.9811	0.0291	12.6
0.2424	0.1462	−11.3	0.5658	0.2140	−0.4	0.8220	0.1317	2.3	0.9993	0.0116	11.0
x_1 1-Heptyne + $(1 - x_1)$ ETBE											
0.0251	−0.0521	−2.6	0.2251	−0.2853	13.4	0.4950	−0.3739	−11.1	0.8931	−0.1968	2.7
0.0654	−0.1310	−11.1	0.2841	−0.3213	10.2	0.6103	−0.3582	−7.8	0.9350	−0.1468	−9.0
0.1138	−0.1934	−3.3	0.3501	−0.3472	5.7	0.7203	−0.3197	3.7	0.9758	−0.0906	−32.4
0.1452	−0.2305	−2.7	0.4114	−0.3632	−1.3	0.7755	−0.2851	14.4	0.9898	−0.0459	−20.3
0.1752	−0.2636	−5.2	0.4552	0.3700	−6.4	0.8303	−0.2560	7.5	0.9921	−0.0295	−9.5

solubility of ether in water is decreasing up to 330 K and at the higher temperatures is slightly increasing. Such a behavior is frequent in the case of (water + polar substance) mixtures.

3. Excess Molar Volumes of Ethyl 1,1-Dimethylethyl Ether + Hydrocarbon Mixtures at 298.15 K and 308.15 K. The results of density measurements for the pure components are listed in Table 5.

The $V_{\mathrm{m}}^{\mathrm{E}}$ values are given in Tables 6 and 7 for the temperatures 298.15 K and 308.15 K, respectively, together with the deviations $\delta V_{\mathrm{m}}^{\mathrm{E}}$, calculated from the smoothing equation:

$$\delta V_{\mathrm{m}}^{\mathrm{E}}/(\mathrm{cm^3\,mol^{-1}}) = V_{\mathrm{m}}^{\mathrm{E}}/(\mathrm{cm^3\,mol^{-1}}) - x_1(1 - x_1)\sum_{r=0}^{r=k} A_r(2x_1 - 1)^r \quad (7)$$

The values of the parameters A_r have been determined using the method of least squares and are given in Table 8 together with the values of the standard deviations.

All of the $V_{\mathrm{m}}^{\mathrm{E}}$ curves are positive, and most of them are symmetrical. Only the (1-heptyne + ETBE) mixture shows negative deviations from additivity. For ETBE, the $V_{\mathrm{m}}^{\mathrm{E}}$ data increase in the following order: 1-heptyne < hexadecane < tetradecane < dodecane < cyclohexane < hexane < decane < octane. This trend would seem to indicate (i) a more organized packing effect in higher *n*-alkanes + ether mixtures, (ii) breakdown of ether−ether interaction, and (iii) a positive effect due to the stronger specific interactions for systems containing a triple bond (1-heptyne).

Interactions between a polar component and an ether seem to occur via complex formation between the two species or n−π interaction (Domańska, 1997; Letcher and Domańska, 1997), and the excess molar volume is usually reported as large and negative. The excess molar volumes

Table 8. Coefficients of Eq 1 and Standard Deviations σ for V_m^E of Binary Mixtures of x_1Hydrocarbon + (1 − x_1)ETBE at the Temperatures 298.15 K and 308.15 K

component	A_0	A_1	A_2	A_3	A_4	$10^3\sigma$/(cm^3 mol^{-1})
			298.15 K			
hexane	0.8988	0.0223				4.1
octane	1.3340	0.1012	0.0902			8.4
decane	0.9364	0.0443				4.6
dodecane	0.6647	0.1037	−0.5946	0.2609	0.6611	2.7
tetradecane	0.5500	0.0633	−0.2732	0.0752		7.0
hexadecane	0.4906	0.0795	−0.0773			5.1
cyclohexane	0.7443	0.0043	−0.1511			5.1
1-heptyne	−1.3628	−0.0040	−0.7389	−0.2778		7.2
			308.15 K			
hexane	0.9961	0.0217				7.4
octane	1.4747	−0.0082	0.6573	−0.0085		4.9
decane	1.0275	−0.0424	0.1668	−0.0166		8.0
dodecane	0.7899	0.1261	−0.6030	−0.0487	0.8140	5.3
tetradecane	0.6420	0.0077	−0.4886	0.2997	0.6550	2.2
hexadecane	0.5296	−0.0009	0.0409	0.0367		8.2
cyclohexane	0.8697	0.0236				6.8
1-heptyne	−1.4500	0.1074	−0.8787	−0.3733		12.8

for mixtures of *n*-alkanes with branched ethers are much higher than those for *n*-ethers or even for diisopropyl ether (Treszczanowicz, 1990). Mixtures of an unsaturated hydrocarbon with ethers (1-heptene + MTBE or ETBE or MTAE) or an aromatic hydrocarbon with ethers (toluene + MTBE or ETBE or MTAE) have been found (Domańska, 1997; Letcher and Domańska, 1997) to show stronger specific interactions, mainly due to the different strengths of the n−π interactions between the unshared electron pairs on the oxygen atom of an ether molecule and the double bond of a hydrocarbon. The V_m^E(max) value is −0.345 cm^3 mol^{-1} (at $x = 0.5$ and 298.15 K) for a (1-heptyne + ETBE) mixture, which is a stronger interaction than that in a (1-heptene + ETBE) mixture and a weaker one than that in a (toluene + ETBE) mixture. The excess volumes of (cyclohexane + ETBE) are positive; the V_m^E(max) is 0.189 cm^3 mol^{-1} at equimolar composition (298.15 K). The excess molar volumes V_m^E at 298.15 K are shown in Figure 3.

4. Prigogine−Flory−Patterson (PFP) Theory. The theory of Flory and co-workers (Flory, 1965; Abe and Flory, 1965; Orwoll and Flory, 1967) has been useful in predicting and correlating the thermodynamic properties of binary mixtures, not only of nonpolar molecules such as hydrocarbons and halohydrocarbons but also of (cyclohexane or tetrachloromethane + ether) mixtures (Spanedda et al., 1991; Berti et al., 1989). Prigogine−Flory−Patterson (PFP) theory has been applied to (hydrocarbon + branched chain ether) mixtures in previous works (Domańska, 1997; Letcher and Domańska, 1997) and is applied to the mixtures discussed in this work using the same procedure as before (Letcher and Baxter, 1989). The interchange parameter X_{12}, which minimized V_m^E experimental data, was adjusted and then used to calculate H_m^E. The pure component parameters, the cubic expansion coefficient α, and the isothermal compressibility κ_T needed for calculations are shown in Table 9. The results of the computations are summarized in Tables 10 and 11, where the parameter X_{12} and predicted $H_m^E(x{=}0.5)$ values are given together with the experimental values of $V_m^E(x{=}0.5)$ for the presented mixtures. For each mixture, the ratio s_1/s_2 of the contact molecular surface areas was estimated from the characteristic volumes of the components using the simple assumption that the molecules are spherical. The results of prediction of $V_m^E(x{=}0.5)$ and $H_m^E(x{=}0.5)$ are shown in Figures 4 and 5, respectively.

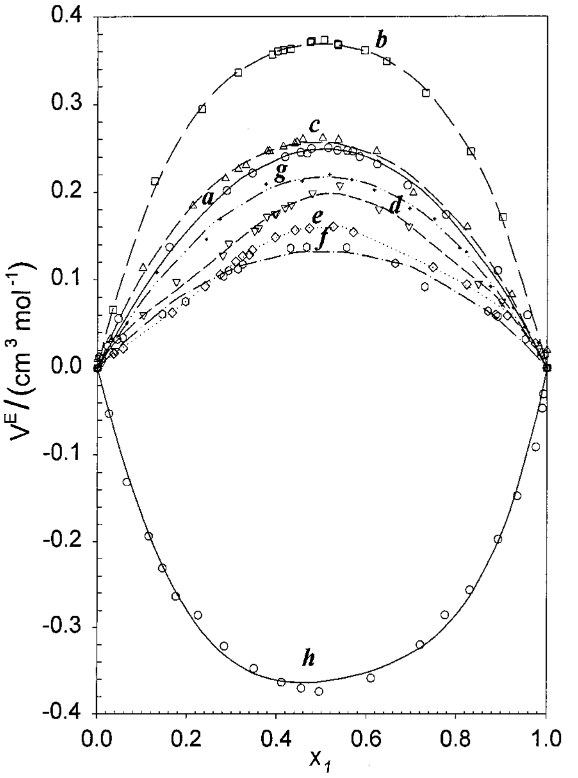

Figure 3. Excess molar volumes V_m^E/(cm^3 mol^{-1}) for hydrocarbon (1) + ETBE (2) mixtures at 298.15 K: ***a***, hexane; ***b***, octane; ***c***, decane; ***d***, dodecane; ***e***, tetradecane; ***f***, hexadecane; ***g***, cyclohexane; ***h***, 1-heptyne. Experimental points are matched by the curves calculated by eq 7.

Table 9. Pure Component Parameters Needed for PFP Theory Calculations

	298.15 K		308.15 K	
component	$10^4\alpha$/K^{-1}	$10^4\kappa_T$/M Pa^{-1}	$10^4\alpha$/K^{-1}	$10^4\kappa_T$/M Pa^{-1}
ETBE	14.28[a]	17.71[a]	14.49[b]	19.17[b]
hexane	13.85[c]	16.85[c]	14.38[d]	18.74[d]
octane	11.64[e]	12.82[e]	11.88[f]	13.60[f]
decane	10.44[g]	11.42[g]	10.64[h]	12.20[i]
dodecane	9.70[e]	10.16[e]	9.90[f]	11.10[i]
tetradecane	9.02[h]	8.72[j]	9.25[h]	10.20[i]
hexadecane	8.84[d]	8.62[d]	9.00[d]	9.30[d]
cyclohexane	12.17[k]	11.20[k]	12.49[k]	12.19[k]
1-heptyne	12.49[l]	12.56[l]	12.62[m]	15.50[m]

[a] Mier et al. (1995). [b] Interpolated from Mier et al. (1995). [c] Heintz (1985). [d] Interpolated from Bender and Heintz (1993). [e] Kaur et al. (1991). [f] Interpolated from Heintz (1985), Kaur et al. (1991), and Funke et al. (1989). [g] Funke et al. (1989). [h] Interpolated from Flory et al. (1964) and Funke et al. (1989). [i] Interpolated from Domańska (1997), Mier et al. (1995), Heintz (1985), Bender and Heintz (1993), and Flory et al. (1964). [j] Zhu et al. (1994b). [k] Aicart et al. (1983). [l] Letcher et al. (1995). [m] Domańska (1997).

It can be seen from Figure 4 and our previous work that the simple PFP theory correctly predicts the sign of V_m^E or H_m^E for most of the (hydrocarbon + branched chain ether) mixtures and is sufficiently accurate in the representation of these excess functions at equimolar concentration; however, some deviations in the symmetry have been observed. There are no H_m^E data for systems formed by hydrocarbons with ETBE. The only comparison can be made with vapor−liquid equilibrium (VLE) data for the system toluene + ETBE published by Steinhagen and Sandler (1994). The results of comparison of the H_m^E calculated from the VLE are shown in Figure 6.

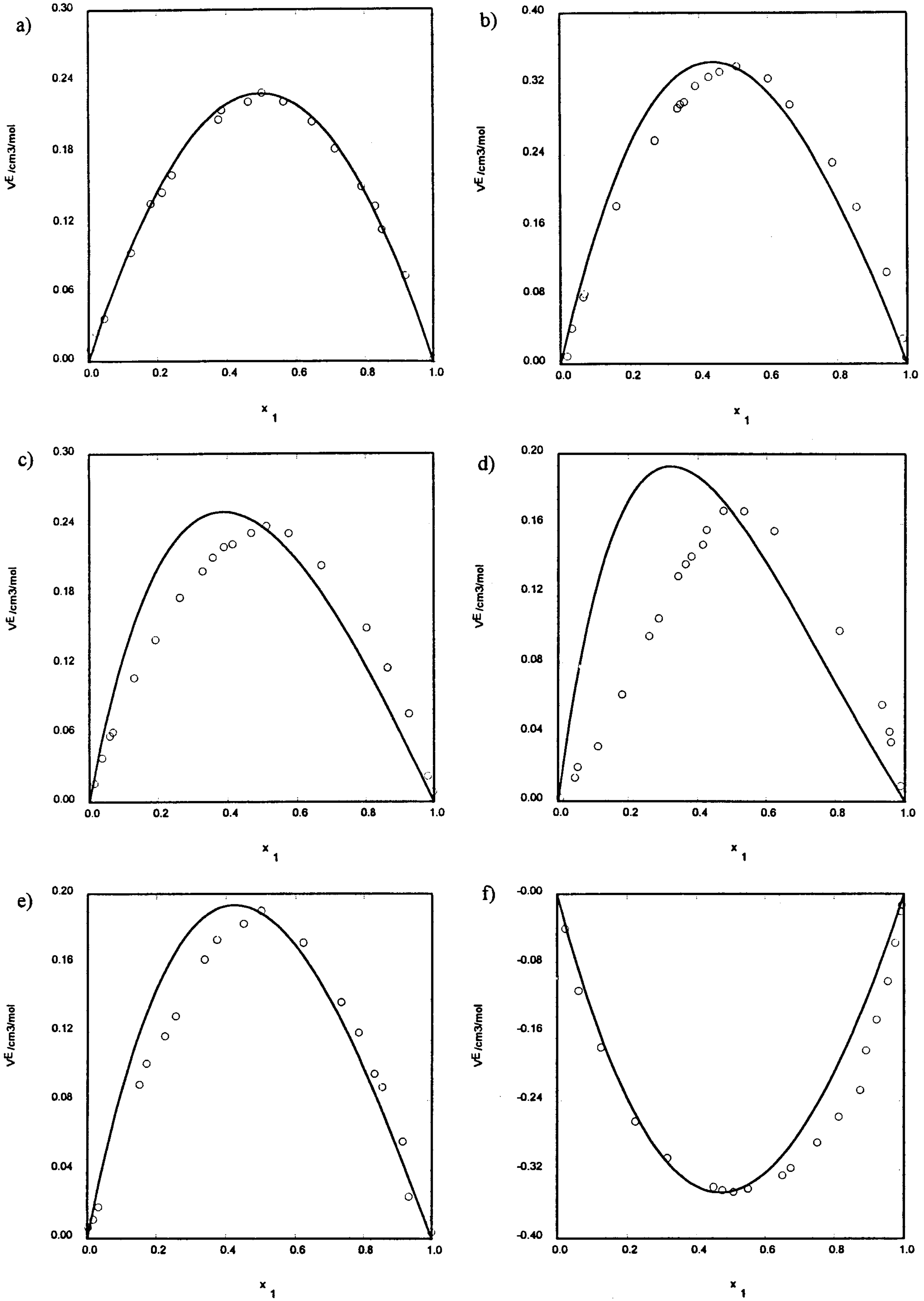

Figure 4. Excess molar volumes V_m^E/(cm^3 mol^{-1}) for hydrocarbon (1) + ETBE (2) mixtures at 298.15 K: ***a***, hexane; ***b***, octane; ***c***, decane; ***d***, dodecane; ***e***, cyclohexane; ***f***, 1-heptyne. Experimental points are matched by the curves calculated by PFP theory.

Table 10. Characteristic Parameters of Pure Components for PFP Theory at 298.15 K and 308.15 K

component	V_{mol}/ (cm^3 mol^{-1})	V^*/ (cm^3 mol^{-1})	T^*/ K	P^*/ (J cm^{-3})
		298.15 K		
ETBE	138.91	104.49	4378	424.8
hexane	131.61	99.65	4446	429.8
octane	163.54	127.99	4856	437.3
decane	195.91	155.90	5109	430.4
dodecane	228.59	184.12	5320	438.8
tetradecane	261.26	212.88	5545	464.5
hexadecane	294.09	240.38	5610	457.7
cyclohexane	124.34	96.35	4270	539.6
1-heptyne	132.04	101.84	4660	498.5
toluene[a]	106.85	84.66	4555	557.7
		308.15 K		
ETBE	140.39	104.65	4431	419.2
hexane	133.11	99.37	4445	424.3
octane	164.90	127.57	4857	449.8
decane	197.32	155.64	5137	431.9
dodecane	230.09	183.71	5339	431.1
tetradecane	262.68	212.07	5543	428.7
hexadecane	295.89	239.93	5630	453.5
cyclohexane	125.46	96.17	4741	537.3
1-heptyne	133.27	101.97	4717	428.6
toluene[a]	107.73	84.72	5090	551.8

[a] Domańska (1997).

Table 11. Exchange Interaction Coefficient X_{12} for the Flory Equation of State Contribution and Experimental V_m^E and Predicted H_m^E Values for Hydrocarbon + ETBE Mixtures at the Equimolar Concentration Using PFP Theory

mixture	X_{12}/(J cm^{-3})	V_m^E/(cm^3 mol^{-1})	H_m^E/(J mol^{-1})
	298.15 K		
ETBE +			
hexane	7.13	0.229	192
octane	14.51	0.339	445
decane	14.18	0.238	475
dodecane	17.29	0.167	633
tetradecane	27.15	0.142	1091
hexadecane	26.28	0.126	1127
cyclohexane	17.85	0.189	462
1-heptyne	−5.82	−0.345	−165
	308.15 K		
ETBE +			
hexane	7.01	0.250	191
octane	15.83	0.372	490
decane	15.10	0.261	510
dodecane	16.88	0.201	619
tetradecane	19.28	0.160	759
hexadecane	26.12	0.142	1122
cyclohexane	17.42	0.218	454
1-heptyne	−9.18	−0.373	−257

Conclusions

The phenomenon of the solid−solid-phase transition of long chain *n*-alkanes has been observed from the solubility curves. The best results for the correlation of experimental points in binary systems of *n*-alkanes in MTBE were obtained by means of the two-parameter NRTL equation with the root-mean-square deviation $\sigma_T = 0.46$ K.

The observed molar excess volumes exhibit an interesting dependence with respect to the *n*-alkane carbon number. Excess volumes increase with increasing *n*-alkane length up to octane, for which the highest positive V_m^E is observed. For higher *n*-alkanes this tendency is reversed and excess volumes decrease with increasing *n*-alkane size. A similar phenomenon was reported for (*n*-alkane + dipropyl ether) by Wang et al. (1989) and for (*n*-alkane + TAME) by Witek et al. (1997). The order of the increase in V_m^E depends of the possible shape of the *n*-alkane chain in the solution. A more organized packing effect in longer than octane hydrocarbons is observed. The predicted molar excess enthalpies increase with increasing *n*-alkane carbon chain, which was observed previously for diisopropyl ether (Zhu et al., 1994a) and for TAME (Zhu et al., 1994b). The calculated molar excess enthalpy for 1-heptyne is negative, showing strong interaction with ETBE.

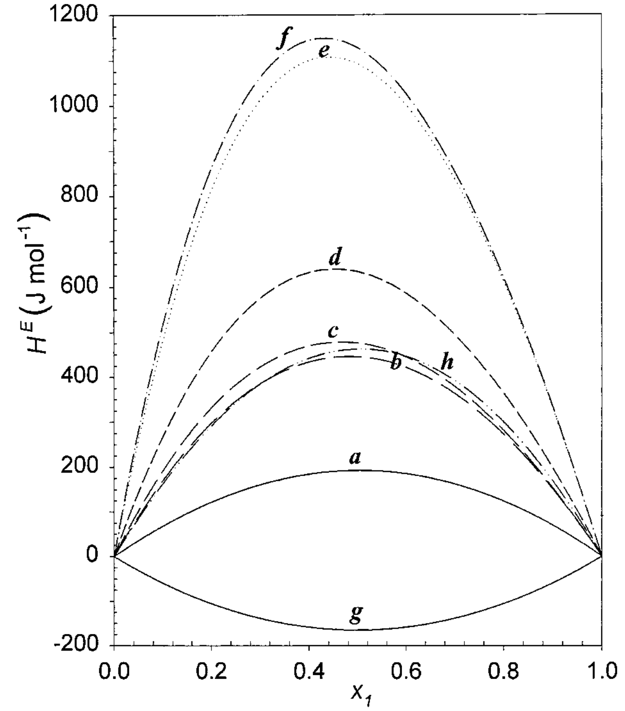

Figure 5. Excess molar enthalpies H_m^E/(J mol $^{-1}$) for hydrocarbon (1) + ETBE (2) mixtures at 298.15 K predicted by PFP theory: ***a***, hexane; ***b***, octane; ***c***, decane; ***d***, dodecane; ***e***, tetradecane; ***f***, hexadecane; ***g***, cyclohexane; ***h***, 1-heptyne.

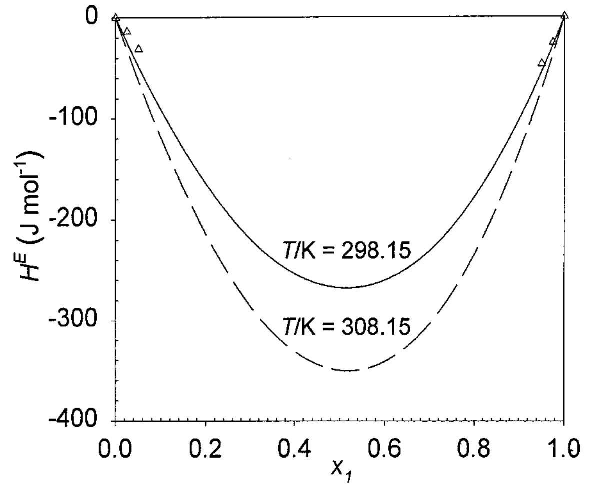

Figure 6. Comparison of excess molar enthalpies H_m^E/(J mol $^{-1}$) for toluene (1) + ETBE (2) mixtures predicted by PFP (lines) and calculated from vapor−liquid equilibrium data (triangles) from Steinhagen and Sandler (1994).

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