Experimental (Solid + Liquid) and (Liquid + Liquid) Equilibria and Excess Molar Volume of Alkanol + Acetonitrile, Propanenitrile, and Butanenitrile Mixtures[†]

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(Solid + liquid) and (liquid + liquid) phase diagrams have been determined for (1-octanol, 1-nonanol, 1-decanol, or 1-undecanol + acetonitrile, propanenitrile, or butanenitrile) mixtures. Only mixtures with acetonitrile show immiscibility in the liquid phase with an upper critical solution temperature. The excess molar volumes (V_m^E) have been determined for a 1-alkanol (1-octanol, 1-nonanol, 1-decanol, or 1-undecanol + propanenitrile) and (1-undecanol + butanenitrile) at 298.15 K and atmospheric pressure. For all the mixtures investigated in this work, the V_m^E is small and positive. Mixtures were investigated in terms of the modified UNIFAC (MU) model using the interaction parameters cited in the literature. The model describes in the correct range of temperature and composition the liquidus curves, critical points, and excess molar enthalpies. The Extended Real Associated Solution (ERAS) and Flory−Benson−Treszczanowicz (FBT) models were also used to represent the V_m^E data and to predict excess molar enthalpies of the investigated systems. Excess molar volumes and enthalpies (literature data) are well-represented by the ERAS model. The ERAS model gives the better prediction than that of the MU model for excess molar enthalpies. The calculated curves using ERAS are closer to the experimental points except in the region of low concentration in alcohol. This means that, in terms of ERAS, the contribution to the excess molar enthalpy from the self-association of the alcohol is overestimated. The MU model underestimates the excess molar enthalpy. The FBT model cannot be used to predict these data as the interaction of the unlike molecules is not described in this model.

Introduction

This paper is a continuation of our systematic study on the interactions between unlike molecules in systems of polar compounds, such as 1-alkanols with amines.[1−4] Mixtures of (alkanol + nitrile) are known from the literature to show weaker interactions than that observed in (1-alkanol + amine), especially for the short-chain alcohols. The measurements of molar excess volumes (V_m^E)[5−15] and molar excess enthalpies (H_m^E)[16,17] for (1-alkanol + acetonitrile) systems were presented previously. Excess molar functions for (1-alkanol + butanenitrile) systems were also presented.[18−25] Excess molar volumes are relatively small and positive in these mixtures (lower than 0.5 $cm^3 \cdot mol^{-1}$), indicating that small structural effects and molar excess enthalpies are large and positive (but less than 2500 $J \cdot mol^{-1}$). From the analysis of the excess molar enthalpy curves, it can be concluded that they are determined mainly by the association of alcohol and by dipolar interactions between nitrile molecules. The ERAS model has already been applied to many binary mixtures of (1-alkanol + nitrile) mixtures.[9,13,25]

In the present work, we extended the thermodynamic study to low temperatures where (solid + liquid) and (liquid + liquid) equilibria were measured. In this work, 1-octanol, 1-nonanol, 1-decanol, and 1-undecanol were chosen in mixtures with acetonitrile, propanenitrile, and butanenitrile. The experimental data of the excess molar volumes of 1-alkanol + nitrile mixtures: (1-octanol, 1-nonanol, 1-decanol, or 1-undecanol + propanenitrile) and (1-undecanol + butanenitrile) at 298.15 K and atmospheric pressure were also measured. The data of V_m^E together with the literature values published previously[20,24] were used for testing the extended real associated solution (ERAS) model, the Flory−Benson−Treszczanowicz (FBT) model, and the modified UNIFAC (MU) model. The ERAS model combines the real association solution model[26−30] with a physical term from Flory's equation of state.[31] The FBT model has been applied first to the excess volumes of binary systems formed by mixing a polar substance base with an alkane or cycloalkanes.[32,33] Result of applied ERAS model and FBT model are compared with results from the MU model.[34]

Experimental Section

The origin of the chemicals and their mass fraction purities were as follows: acetonitrile (Aldrich Chemical Co., 99.93 %), propanenitrile (Fluka, >99 %), butanenitrile (Fluka, >99 %), 1-octanol (Aldrich Chemical Co., 99+ %), 1-nonanol (Fluka, >98 %), 1-decanol (Aldrich Chemical Co., 99 %), and 1-undecanol (Fluka, >98 %). Nitriles and 1-alkanols were fractionally distilled over different drying reagents to mass fraction purity better than 99.8 % determined by GLC. Liquids were stored over freshly activated molecular sieves of type 4 Å (Union Carbide). The physical properties of the substances used in this work are listed in Table 1 together with the literature values.

The (solid + liquid) and (liquid + liquid) equilibrium temperatures were determined using a visual method.[43]

[†] Presented at 21st European Symposium on Applied Thermodynamics, June 1−5, 2005, Jurata, Poland.

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10.1021/je050262m CCC: $30.25

Table 1. Physical Properties of the Pure Substances

compound	V_m cm^3·mol^{-1}	T_{fus} K	$T_{fus}^{(lit)}$ K	ρ g·cm^{-3}	$\rho^{(lit)}$ g·cm^{-3}	$\Delta_{fus}H$ kJ·mol^{-1}	$\Delta_{fus}C_{p,1}$ J·mol^{-1}·K^{-1}
1-octanol	158.41	258.03	258.35[a]	0.82221	0.82250[b]	23.70[a]	41.33[a]
1-nonanol	174.95	268.10	268.00[c]	0.82460	0.82384[d]	24.54[e]	55.78[e]
1-decanol	191.49	278.67	279.14[f]	0.82664	0.82623[g]	31.40[e]	82.65[e]
1-undecanol	207.77	289.63	289.65[h]	0.82934	0.82898[d]	30.59[e]	76.52[e]
acetonitrile	52.87	230.42	231.56[i]				
propanenitrile	70.90		180.37[j]	0.77705	0.77682[j]		
butanenitrile	87.86		161.30[j]	0.78657	0.78660[k]		

[a] Ref 35. [b] Ref 28. [c] Ref 36. [d] Ref 37. [e] Ref 4. [f] Ref 38. [g] Ref 39. [h] Ref 40. [i] Ref 41. [j] Ref 42. [k] Ref 25.

Table 2. Experimental (Solid + Liquid) Phase Equilibria[a]

x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K	x_1	T/K
1-Octanol (1) + Acetonitrile (2)															
0.0000	230.42	0.0661	255.53	0.1966	255.53	0.3611	255.53	0.5032	255.53	0.6752	255.53	0.8315	255.82	1.0000	258.03
0.0100	246.88	0.0847	255.53	0.2315	255.53	0.3939	255.53	0.5242	255.53	0.6983	255.53	0.8733	256.02		
0.0226	253.45	0.1025	255.53	0.2721	255.53	0.4220	255.53	0.5593	255.53	0.7357	255.53	0.9119	256.41		
0.0324	255.34	0.1320	255.53	0.2953	255.53	0.4680	255.53	0.5848	255.53	0.7708	255.53	0.9458	256.93		
0.0454	255.53	0.1586	255.53	0.3315	255.53	0.4842	255.53	0.6372	255.53	0.7948	255.53	0.9677	257.42		
1-Nonanol (1) + Acetonitrile (2)															
0.0000	230.42	0.0555	264.27	0.1572	264.27	0.3021	264.27	0.4607	264.27	0.6008	264.27	0.7427	264.27	0.8865	265.61
0.0091	253.08	0.0678	264.27	0.2007	264.27	0.3389	264.27	0.4981	264.27	0.6270	264.27	0.7690	264.43	0.9164	266.04
0.0161	260.48	0.0835	264.27	0.2298	264.27	0.3703	264.27	0.5371	264.27	0.6700	264.27	0.7996	264.47	0.9588	266.84
0.0242	264.09	0.0986	264.27	0.2653	264.27	0.4229	264.27	0.5731	264.27	0.7097	264.27	0.8395	264.72	1.0000	268.10
0.0388	264.27	0.1199	264.27												
1-Decanol (1) + Acetonitrile (2)															
0.0000	230.42	0.0371	276.45	0.1562	276.45	0.2763	276.45	0.4170	276.45	0.6250	276.45	0.8095	277.13	1.0000	278.67
0.0063	264.74	0.0451	276.45	0.1850	276.45	0.3152	276.45	0.4860	276.45	0.6671	276.45	0.8605	277.61		
0.0130	270.55	0.0740	276.45	0.2143	276.45	0.3429	276.45	0.5382	276.45	0.6920	276.45	0.9098	278.23		
0.0218	275.58	0.1077	276.45	0.2440	276.45	0.3769	276.45	0.5719	276.45	0.7465	276.64	0.9513	278.36		
1-Undecanol (1) + Acetonitrile (2)															
0.0000	230.42	0.0567	285.20	0.1687	285.20	0.3210	285.20	0.4999	285.20	0.6210	285.20	0.7548	286.16	0.8954	288.04
0.0072	274.93	0.0838	285.20	0.1871	285.20	0.3722	285.20	0.5338	285.20	0.6527	285.20	0.7891	286.78	0.9298	288.70
0.0197	283.81	0.1044	285.20	0.2037	285.20	0.4162	285.20	0.5597	285.20	0.6895	285.48	0.8311	287.21	0.9644	289.17
0.0401	285.20	0.1366	285.20	0.2707	285.20	0.4689	285.20	0.5983	285.20	0.7186	285.89	0.8678	287.62	1.0000	289.63
1-Octanol (1) + Propanenitrile (2)															
0.0000	180.37[b]	0.0449	246.37	0.1040	251.44	0.2239	253.63	0.4082	253.76	0.6143	254.03	0.7722	254.76	0.9187	256.67
0.0275	240.39	0.0557	248.02	0.1390	252.64	0.2855	253.64	0.4677	253.79	0.6558	254.10	0.8080	254.94	0.9488	257.26
0.0310	243.21	0.0866	250.15	0.1822	253.51	0.3460	253.71	0.5573	253.88	0.7098	254.38	0.8573	255.53	1.0000	258.03
1-Nonanol (1) + Propanenitrile (2)															
0.0000	180.37[b]	0.0454	255.81	0.1104	261.05	0.2388	262.56	0.4137	262.66	0.5776	262.83	0.7535	263.74	0.9047	265.57
0.0143	246.22	0.0561	257.29	0.1447	261.74	0.2956	262.61	0.4706	262.67	0.6363	262.99	0.8028	264.15	0.9629	266.75
0.0200	250.68	0.0679	258.69	0.1964	262.37	0.3589	262.64	0.5372	262.77	0.6900	263.31	0.8604	264.89	1.0000	268.10
0.0332	253.74	0.0882	260.30												
1-Decanol (1) + Propanenitrile (2)															
0.0000	180.37[b]	0.0500	270.57	0.1948	273.92	0.3668	274.28	0.5697	274.79	0.7228	275.53	0.8648	277.29	0.9619	278.32
0.0119	259.84	0.0977	272.82	0.2576	273.99	0.4144	274.37	0.6489	275.05	0.7920	276.17	0.9257	278.00	1.0000	278.67
0.0244	265.73	0.1360	273.79	0.3104	274.12	0.4794	274.53								
1-Undecanol (1) + Propanenitrile (2)															
0.0000	180.37[b]	0.0533	277.51	0.1528	281.73	0.3398	282.94	0.5103	283.46	0.7071	284.69	0.8544	286.46	0.9430	288.73
0.0129	266.07	0.0803	279.63	0.1996	282.37	0.3946	283.11	0.5740	283.72	0.7793	285.28	0.9009	287.57	1.0000	289.63
0.0265	272.28	0.1171	281.12	0.2662	282.76	0.4469	283.21	0.6537	284.15						
1-Octanol (1) + Butanenitrile (2)															
0.0000	161.30[b]	0.0439	241.00	0.1309	248.27	0.2943	251.30	0.4797	252.67	0.6624	253.33	0.8386	255.06	0.9677	257.27
0.0172	230.58	0.0529	242.88	0.1687	249.46	0.3464	251.73	0.5338	252.86	0.7186	253.80	0.8757	255.52	1.0000	258.03
0.0228	234.33	0.0740	244.96	0.2035	250.14	0.3951	252.18	0.5691	252.99	0.7540	254.01	0.8998	255.71		
0.0318	237.67	0.1052	247.06	0.2450	250.83	0.4329	252.36	0.6164	253.19	0.7890	254.47	0.9290	256.24		
1-Nonanol (1) + Butanenitrile (2)															
0.0000	161.30[b]	0.0346	248.00	0.1414	257.81	0.2569	260.15	0.4198	261.26	0.6035	262.31	0.7607	263.47	0.8752	264.91
0.0134	233.30	0.0479	251.24	0.1819	258.90	0.2888	260.31	0.4672	261.50	0.6420	262.51	0.7968	263.79	0.9233	265.79
0.0201	237.15	0.0791	254.88	0.2051	259.51	0.3321	260.58	0.5275	261.82	0.6755	262.79	0.8292	264.15	0.9631	266.97
0.0250	242.88	0.1145	256.64	0.2325	259.91	0.3695	260.89	0.5669	262.06	0.7146	263.06	0.8612	264.54	1.0000	268.10
1-Decanol (1) + Butanenitrile (2)															
0.0000	161.30[b]	0.0523	263.37	0.1328	269.39	0.2967	272.43	0.4672	273.57	0.6513	275.19	0.8447	277.19	1.0000	278.67
0.0172	253.42	0.0669	265.36	0.1710	270.59	0.3325	272.63	0.5222	273.84	0.7116	276.02	0.8955	277.69		
0.0240	256.66	0.0820	266.77	0.2088	271.34	0.3895	273.16	0.5607	274.05	0.7518	276.36	0.9395	278.30		
0.0354	260.02	0.1012	267.98	0.2540	271.98	0.4261	273.34	0.6004	274.44	0.7952	276.72	0.9640	278.50		
1-Undecanol (1) + Butanenitrile (2)															
0.0000	161.30[b]	0.0501	271.77	0.1814	279.42	0.3570	281.96	0.5846	283.53	0.7188	285.15	0.8640	287.15	1.0000	289.63
0.0141	257.30	0.0807	275.00	0.2222	280.21	0.4061	282.37	0.6180	283.83	0.7596	285.58	0.8984	287.81		
0.0246	265.44	0.1094	276.73	0.2668	281.07	0.4761	282.86	0.6534	284.42	0.7930	285.97	0.9335	288.39		
0.0373	269.51	0.1366	278.11	0.3146	281.62	0.5242	283.30	0.6887	284.82	0.8319	286.57	0.9682	289.05		

[a] T denotes the equilibrium temperature. [b] Ref 42.

Appropriate mixtures of solute and solvent were heated very slowly (less than $1.0 \cdot 10^{-3}$ K·h^{-1} near the equilibrium temperature) with continuous stirring inside a Pyrex glass cell, which was placed in a glass thermostat filled with

Table 3. Experimental (Liquid + Liquid) Equilibrium Data for {x_1 1-Alkanol + $(1 - x_1)$ Nitrile}: x_1^*, Values Calculated at Constant Temperature for the Experimental Point in the 1-Alkanol Rich Phase or Nitrile Rich Phase

x_1	x_1^*	T/K	x_1	x_1^*	T/K
1-Octanol (1) + Acetonitrile (2)					
0.0454	0.7618	262.13	0.4220	0.1696	280.60
0.0661	0.6659	270.06	0.4680	0.1460	279.59
0.0847	0.6069	273.89	0.4842	0.1362	279.12
0.1025	0.5461	276.89	0.5032	0.1235	278.37
0.1320	0.4923	278.80	0.5242	0.1143	277.69
0.1586	0.4358	280.25	0.5593	0.0968	276.33
0.1966	0.3765	281.31	0.5848	0.0871	274.81
0.2315	0.3140	281.93	0.6372	0.0749	272.25
0.2721	0.2528	282.07	0.6752	0.0637	269.33
0.2953	0.2431	282.03	0.6983	0.0610	267.62
0.3315	0.2211	281.83	0.7357	0.0522	264.93
0.3611	0.2063	281.56	0.7708	0.0418	260.70
0.3939	0.1876	281.08	0.7948	0.0399	257.40
1-Nonanol (1) + Acetonitrile (2)					
0.0388	0.7675	267.51	0.3703	0.1691	289.36
0.0555	0.6799	275.27	0.4229	0.1420	288.39
0.0678	0.5910	280.74	0.4607	0.1246	287.49
0.0835	0.5462	283.66	0.4981	0.1033	285.76
0.0986	0.5097	285.33	0.5371	0.0891	284.28
0.1199	0.4678	287.24	0.5731	0.0742	282.18
0.1572	0.3879	289.08	0.6008	0.0648	280.19
0.2007	0.3196	290.00	0.6270	0.0590	278.66
0.2298	0.2853	290.27	0.6700	0.0541	276.18
0.2653	0.2518	290.33	0.7097	0.0498	272.76
0.3021	0.2169	290.18	0.7427	0.0439	270.09
0.3389	0.1911	289.86			
1-Decanol (1) + Acetonitrile (2)					
0.0371	0.6979	277.56	0.3429	0.1730	296.53
0.0451	0.6541	283.77	0.3769	0.1494	296.02
0.0740	0.5432	290.99	0.4170	0.1298	295.29
0.1077	0.4685	293.88	0.4860	0.0989	293.18
0.1562	0.3662	296.24	0.5382	0.0768	291.38
0.1850	0.3209	296.71	0.5719	0.0660	288.91
0.2143	0.2968	296.94	0.6250	0.0498	285.57
0.2440	0.2603	297.05	0.6671	0.0431	282.88
0.2763	0.2284	297.01	0.6920	0.0369	278.80
0.3152	0.1929	296.77			
1-Undecanol (1) + Acetonitrile (2)					
0.0401	0.6289	290.07	0.3722	0.0963	301.08
0.0567	0.5312	295.38	0.4162	0.0816	300.06
0.0838	0.4060	300.32	0.4689	0.0737	298.47
0.1044	0.3534	301.46	0.4999	0.0666	297.20
0.1366	0.2926	302.59	0.5338	0.0571	295.23
0.1687	0.2546	303.08	0.5597	0.0540	294.28
0.1871	0.2393	303.21	0.5983	0.0459	292.27
0.2037	0.2227	303.25	0.6210	0.0428	290.77
0.2707	0.1515	302.89	0.6527	0.0299	288.18
0.3210	0.1197	302.19			

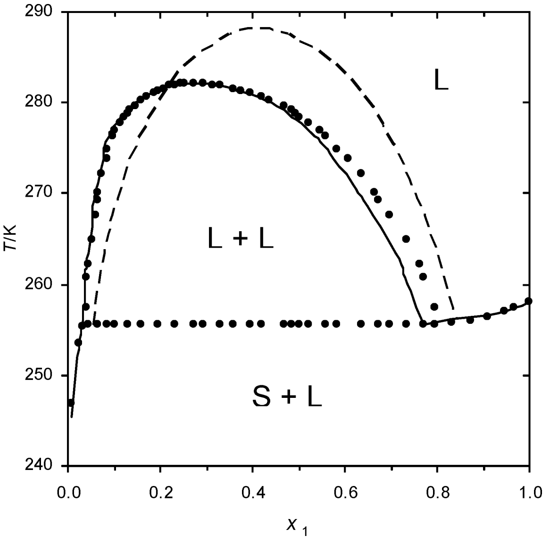

Figure 1. Phase diagram for 1-octanol (1) + acetonitrile (2). Points, experimental equilibrium temperatures; solid line, NRTL equation; dashed line, modified UNIFAC (MU) results.

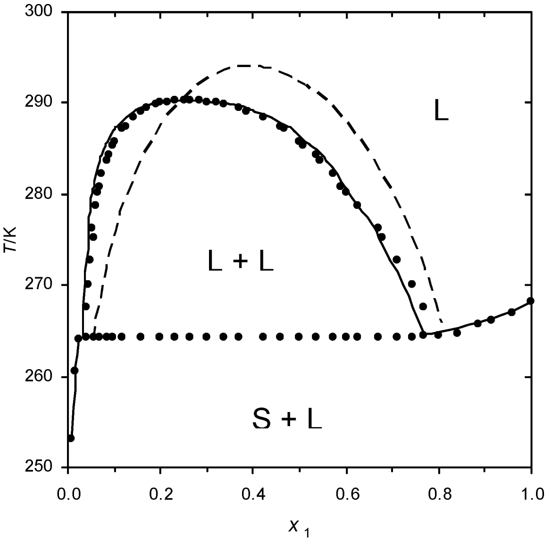

Figure 2. Phase diagram for 1-nonanol (1) + acetonitrile (2). Points, experimental equilibrium temperatures; solid line, NRTL equation; dashed line, modified UNIFAC (MU) results.

acetone and dry ice. The temperature at which the last crystals disappeared (or disappearance of solution cloudiness) was taken as the temperature of the (solid + liquid) equilibrium. The crystal disappearance temperatures were detected visually. In (liquid + liquid) measurements, the disappearance two phases in the middle of the liquid phase was observed as temperature increased. The temperature was measured with an electronic thermometer P 550 (Dostmann Electronic GmbH) with the probe totally immersed in the thermostating liquid. The thermometer was calibrated on the basis of ITS-90. The uncertainty of the temperature measurements was ± 0.05 K, and that of the mole fraction did not exceed ± 0.0005.

The densities of all the chemicals were measured using an Anton Paar DMA 602 vibrating-tube densimeter thermostated at $T = (298.15 \pm 0.01)$ K. The densimeter's calibration was performed at atmospheric pressure using double-distilled and degassed water, specially purified benzene (Chemipan, Poland 0.999) and dried air. The vibrating-tube temperature was measured by an Anton Paar DM 100-30 digital thermometer and was regulated to within better than ± 0.01 K using a Unipan 60 thermostat and 202 temperature control system (Unipan, Poland). Mixtures were prepared by mass with the error in mole fraction being estimated as $< 5 \times 10^{-5}$. The uncertainty of the density measurements was ± 0.0005 $g \cdot cm^{-3}$. The densities of the nitriles and the 1-alkanols are in satisfactory agreement with the literature values, (shown in Table 1).

Results and Discussion

SLE and LLE. Experimental data of the (solid + liquid) and (liquid + liquid) equilibrium temperatures of {1-alkanol (1) + nitrile (2)} mixtures are recorded in Tables 2 and 3 and are shown in Figures 1 to 5. In this study, simple eutectic mixtures with complete immiscibility in the solid phase were assumed. Even the eutectic points were at very low temperatures and were not detected. For the

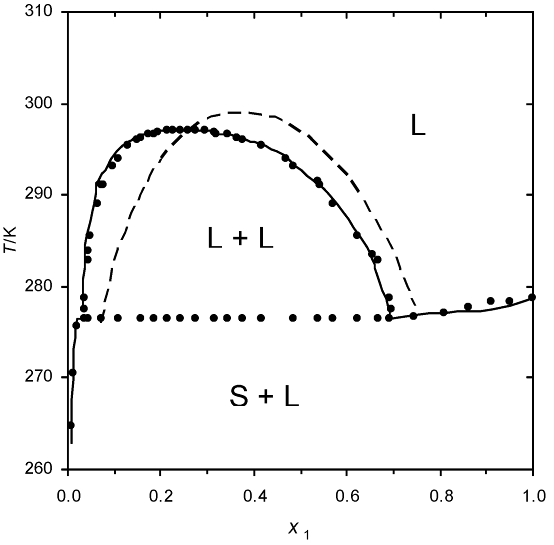

Figure 3. Phase diagram for 1-decanol (1) + acetonitrile (2). Points, experimental equilibrium temperatures; solid line, NRTL equation; dashed line, modified UNIFAC (MU) results.

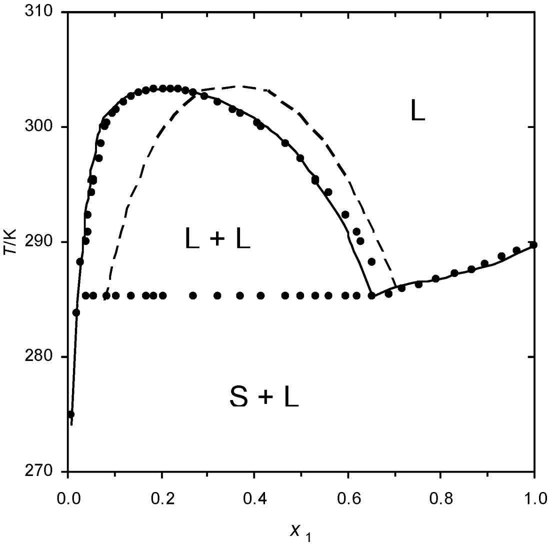

Figure 4. Phase diagram for 1-undecanol (1) + acetonitrile (2). Points, experimental equilibrium temperatures; solid line, NRTL equation; dashed line, modified UNIFAC (MU) results.

systems (1-alkanol + propanenitrile or butanenitrile), the observed solubility decreases with an increase of the melting temperature of the 1-alkanol. The liquidus curves are almost parallel for different alcohols and show complete miscibility in the liquid phase (see Figure 5 as an example). By increasing the alkyl chain length of 1-alkanol, the composition of the eutectic point shifts to the lower 1-alkanol mole fraction.

Our results of LLE are very similar to results published earlier for two systems (1-decanol or 1-undecanol + acetonitrile).[44] The UCST are 297.06 K ($x_1 = 0.252$) and 303.26 K ($x_1 = 0.216$) for 1-decanol and 1-undecanol, respectively, which is not far from 296.2 K for 1-decanol[44] and 302.2 K for 1-undecanol.[44] For two other mixtures the UCSTs were 282.08 ($x_1 = 0.266$) and 290.33 K ($x_1 = 0.258$) for 1-octanol and 1-nonanol, respectively. By increasing the alkyl chain length of 1-alkanol, the UCST increases and shifs to the lower 1-alkanol mole fraction.

Excess Molar Volumes. Experimental data of the V_m^E of (1-alkanol + nitrile) are recorded in Table 4 together with

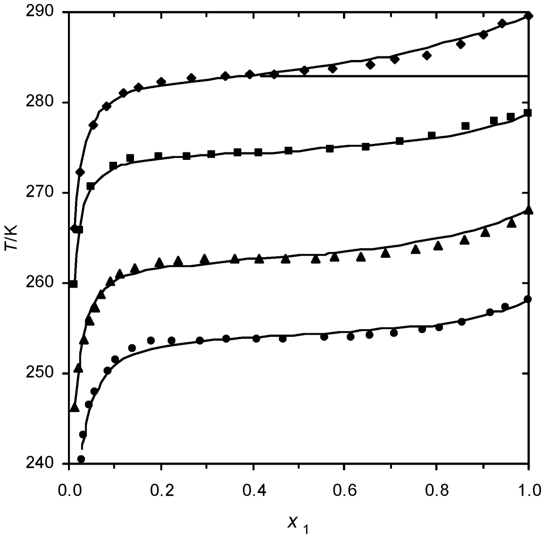

Figure 5. (Solid + liquid) for 1-alkanol (1) + propanenitrile (2). Points, experimental equilibrium temperatures: ●, 1-octanol; ▲, 1-nonanol; ■, 1-decanol; ◆, 1-undecanol. Solid line, Wilson equation.

Table 4. Experimental Data of Excess Molar Volume (V_m^E) and Deviations (δV_m^E) at 298.15 K

x_1	V_m^E / $\mathrm{cm^3 \cdot mol^{-1}}$	$10^{-3}\,\delta V_m^E$ / $\mathrm{cm^3 \cdot mol^{-1}}$	x_1	V_m^E / $\mathrm{cm^3 \cdot mol^{-1}}$	$10^{-3}\,\delta V_m^E$ / $\mathrm{cm^3 \cdot mol^{-1}}$
		1-Octanol (1) + Propanenitrile (2)			
0.0519	0.0801	7.2	0.5417	0.2554	−6.3
0.1152	0.1480	2.6	0.6160	0.2292	−4.8
0.1847	0.2107	5.0	0.6786	0.2021	−1.8
0.3252	0.2728	0.0	0.8161	0.1343	12.0
0.4431	0.2794	−0.2	0.9081	0.0662	4.9
		1-Nonanol (1) + Propanenitrile (2)			
0.0813	0.1433	7.0	0.5911	0.2733	5.1
0.1866	0.2518	5.0	0.6946	0.2268	6.0
0.2941	0.2944	−6.7	0.7915	0.1641	−0.8
0.3686	0.3069	−6.1	0.8633	0.1103	−5.8
0.4752	0.3038	0.2	0.9655	0.0271	−5.6
		1-Decanol (1) + Propanenitrile (2)			
0.0595	0.1240	1.2	0.5065	0.3348	2.7
0.1418	0.2369	3.5	0.5865	0.3102	2.7
0.1984	0.2757	−5.5	0.6745	0.2604	−3.2
0.2662	0.3203	3.0	0.7772	0.1877	−3.1
0.3447	0.3350	−3.3	0.8541	0.1276	3.0
0.4183	0.3431	0.2	0.9513	0.0389	0.9
		1-Undecanol (1) + Propanenitrile (2)			
0.0489	0.1211	18.5	0.5378	0.3701	3.9
0.1145	0.2167	6.1	0.6645	0.3169	11.5
0.1814	0.2859	−4.4	0.7598	0.2422	2.1
0.2654	0.3502	−3.8	0.8341	0.1690	−9.2
0.3574	0.3792	−7.0	0.9435	0.0603	−7.3
0.4258	0.3868	−2.9			
		1-Undecanol (1) + Butanenitrile (2)			
0.0376	0.0780	10.4	0.5242	0.3862	−0.1
0.1580	0.2445	6.5	0.6185	0.3436	−7.3
0.2846	0.3401	−7.2	0.7218	0.2851	0.1
0.3587	0.3790	−2.2	0.8356	0.1902	5.5
0.4259	0.4003	5.8	0.9612	0.0549	7.8

the deviations (δV_m^E) calculated from the smoothing Redlich−Kister equation:

$$\delta V_m^E = V_m^E - x_1(1 - x_1)\sum_{r=0}^{r=3} B_r/(\mathrm{cm^3 \cdot mol^{-1}})(2x_1 - 1)^r \quad (1)$$

where x_1 is the mole fraction of the 1-alkanol and $V_m^E/(\mathrm{cm^3 \cdot mol^{-1}})$ is the molar excess volume. The values of the parameters (B_r) have been determined using a method

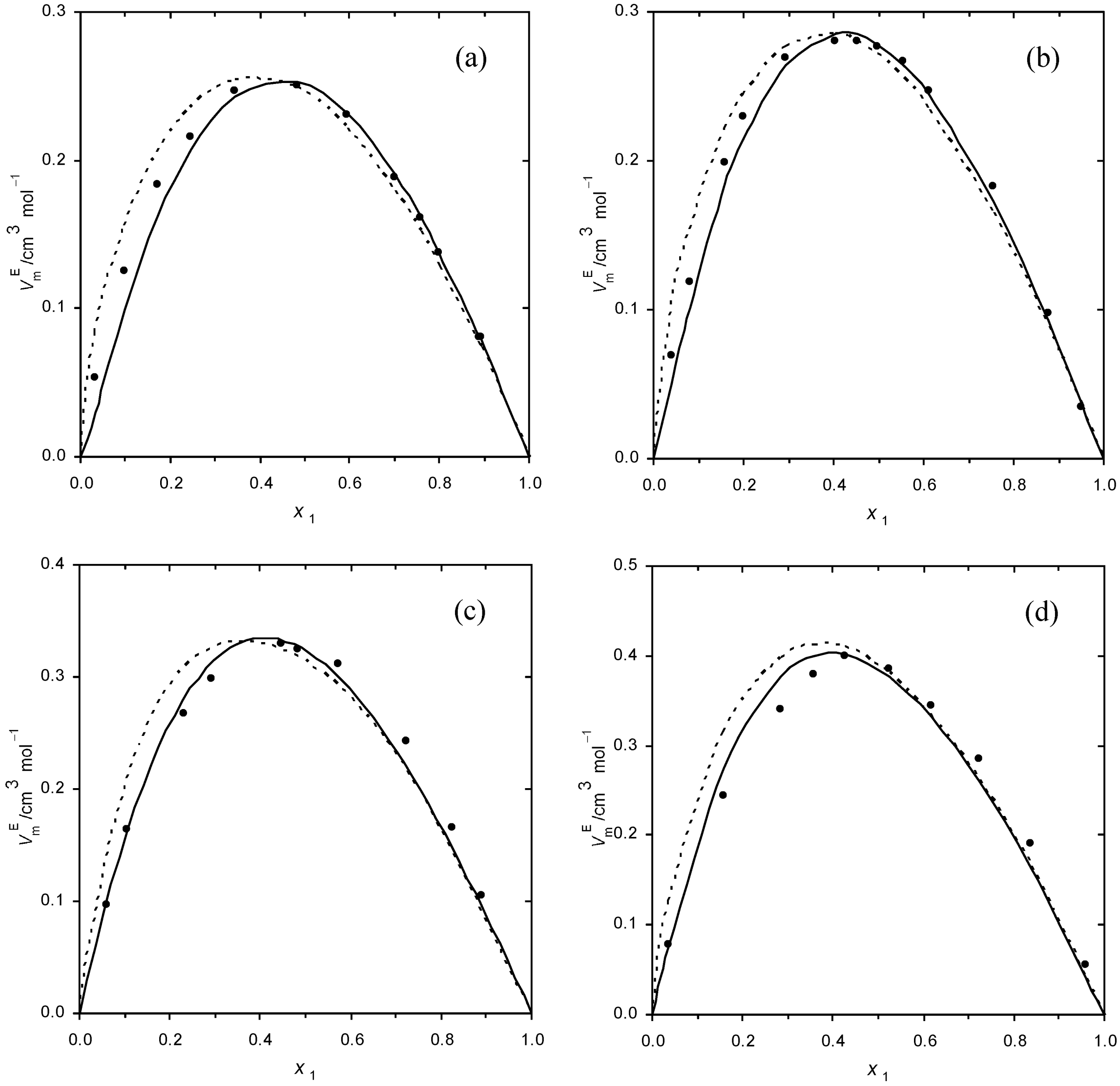

Figure 6. V_m^E for 1-alkanol (1) + butanenitrile (2) mixtures at 298.15 K for (a) 1-octanol (ref 20), (b) 1-nonanol (ref 24), (c) 1-decanol (ref 24), (d) 1-undecanol (this work). Points, experimental results; solid line, ERAS prediction; dotted line, FBT results.

Table 5. Coefficients of the Redlich−Kister Equation and Standard Deviation (σ) for V_m^E of Binary Mixtures of Alkanol (1) + Nitrile (2) at 298.15 K

mixture	B_o cm^3·mol^{-1}	B_1 cm^3·mol^{-1}	B_2 cm^3·mol^{-1}	B_3 cm^3·mol^{-1}	$10^3\ \sigma$ cm^3·mol^{-1}
1-octanol (1) + propanenitrile (2)	1.0906	−0.4364			6.4
1-nonanol (1) + propanenitrile (2)	1.1918	−0.5046	0.2997		6.4
1-decanol (1) + propanenitrile (2)	1.3340	−0.4089	0.2376	−0.4609	3.7
1-undecanol (1) + propanenitrile (2)	1.5108	−0.5199	0.2783		9.8
1-undecanol (1) + butanenitrile (2)	1.5647	−0.3277			6.9

Table 6. $V_{m(max)}^E$ Values and the Mole Fractions ($x_{1(max)}$) for Alkanol (1) + Nitrile (2) Mixtures at 298.15 K

system	$V_{m(max)}^E$/cm^3·mol^{-1}	$x_{1(max)}$
1-octanol + propanenitrile	0.2828	0.4097
1-nonanol + propanenitrile	0.3134	0.3851
1-decanol + propanenitrile	0.3430	0.4075
1-undecanol + propanenitrile	0.3903	0.4070
1-undecanol + butanenitrile	0.3954	0.4493

of least-squares. The parameters are given in Table 5 together with the standard deviation (σ):

$$\sigma = \left\{ \sum_{i=1}^{n} (V_{m(exp)}^E - V_{m(calc)}^E)_i^2/(n-k) \right\}^{1/2} \qquad (2)$$

where n is the number of experimental points and k is the number of coefficients.

The V_m^E is positive for all mixtures over the entire composition range (presented in Figure 6) for 1-alkanol + butanenitrile as an example. The maximum of $V_{m(max)}^E$ occurs over the mole fraction range $0.38 < x_1 < 0.45$. The excess molar volume data for 1-alkanol + propanenitrile increase in the following order: 1-octanol < 1-nonanol < 1-decanol < 1-undecanol. The measured $V_{m(max)}^E$ values and sufficient compositions ($x_{1(max)}$) are plotted in Table 6. Our results are compatible with literature data.[10,20,24]

Correlations and Theories

(Liquid + Liquid) Phase Equilibrium Correlation. In this study one method is used to correlate the solute

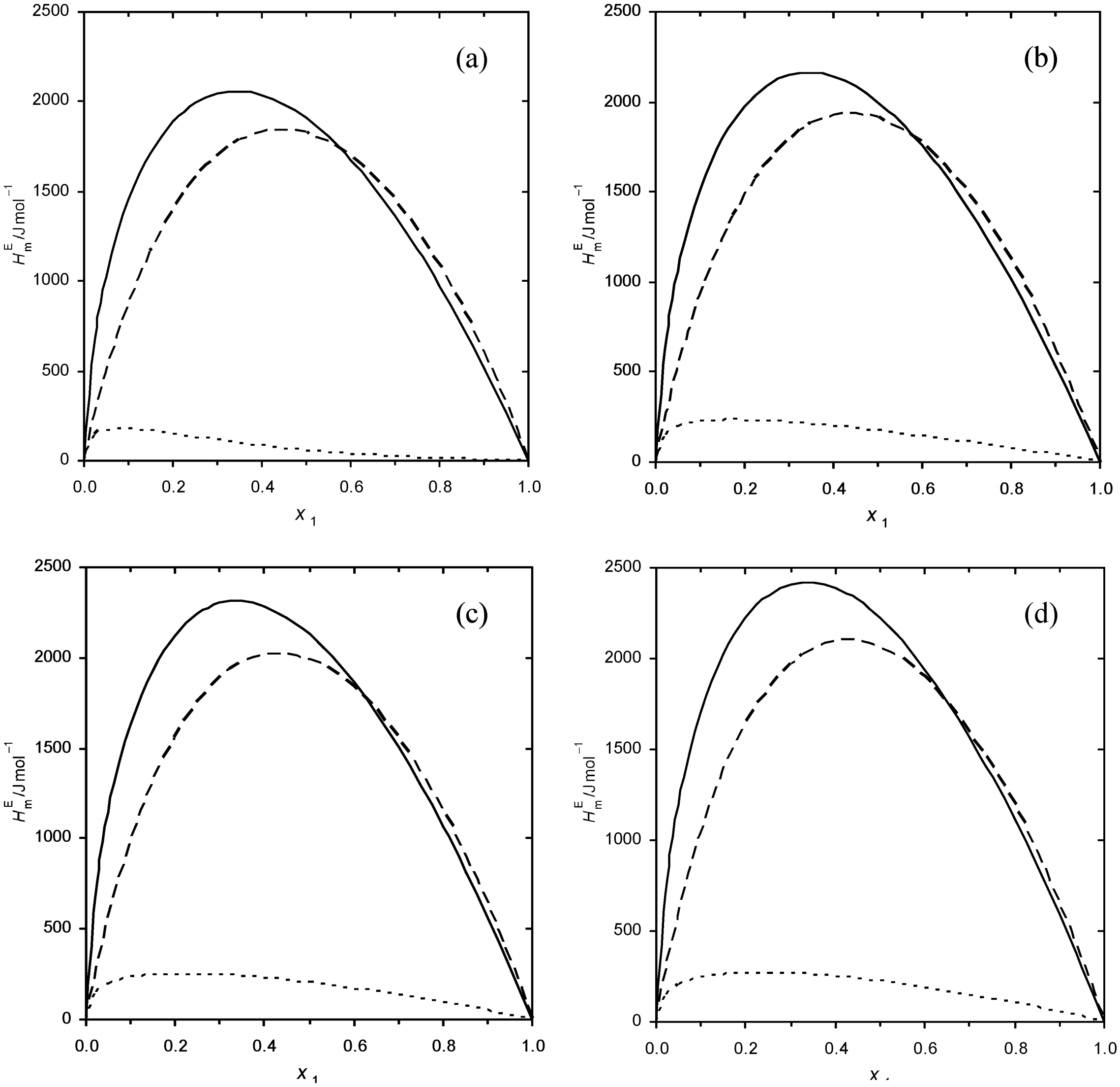

Figure 7. H_m^E for 1-alkanol (1) + propanenitrile (2) mixtures at 298.15 K for (a) 1-octanol, (b) 1-nonanol, (c) 1-decanol, (d) 1-undecanol. Solid line, ERAS prediction; dotted line, FBT results; dashed lines, modified UNIFAC (MU) prediction.

activity coefficients (γ_1) based on the NRTL model describing the excess Gibbs free energy[45]:

$$\frac{G^E}{RT} = x_1x_2\left[\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{G_{12}x_1 + x_2}\right] \tag{3}$$

where

$$\tau_{12} = (g_{12} - g_{22})/RT \tag{4}$$

$$\tau_{21} = (g_{21} - g_{11})/RT \tag{5}$$

$$G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{6}$$

$$G_{21} = \exp(-\alpha_{12}\tau_{21}) \tag{7}$$

The activity coefficients and the model adjustable parameters ($g_{12} - g_{22}$) and ($g_{21} - g_{11}$) were found by minimization of the objective function OF:[46]

$$\mathrm{OF} = \sum_{i=1}^{n}\{(\Delta x_1)_i^2 + (\Delta x_1^*)_i^2\} \tag{8}$$

where n is the number of experimental points and Δx is defined as

$$\Delta x = x_{\mathrm{cal}} - x_{\mathrm{exp}} \tag{9}$$

The root-mean-square deviation of mole fraction was defined as follows:

$$\sigma_x = \left\{\sum_{i=1}^{n}\frac{(\Delta x_1)_i^2}{n-2} + \sum_{i=1}^{n}\frac{(\Delta x_1^*)_i^2}{n-2}\right\}^{1/2} \tag{10}$$

The NRTL equation was used for the correlation of the {1-alkanol (1) + acetonitrile (2)} mixtures to the simultaneous description of SLE and LLE. The calculated values of the equation parameters, and corresponding root-mean-square deviations are presented in Table 7.

(Solid + Liquid) Equilibrium Correlation. For the systems {1-alkanol (1) + propanenitrile or butanenitrile (2)}, three methods were used to derive the solute activity coefficients (γ_1) from the so-called correlation equations that describe the Gibbs excess energy, (G^E): the NRTL1,[47] Wilson,[48] and UNIQUAC ASM.[49] Using these equations a better description was obtained for the SLE correlation than that with the simple NRTL equation. The solubility

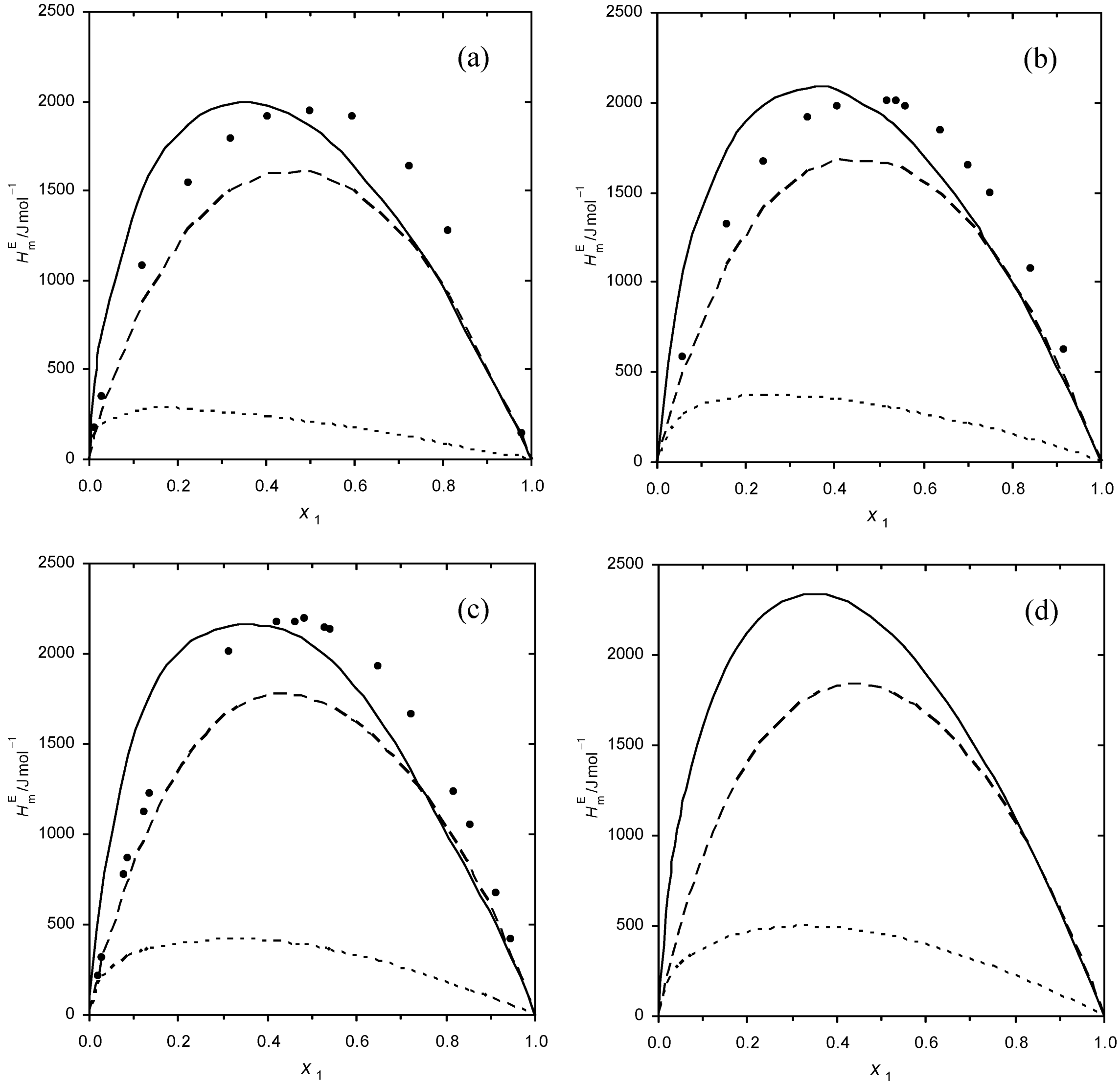

Figure 8. $H_m^E$for 1-alkanol (1) + butanenitrile (2) mixtures at 298.15 K for (a) 1-octanol (ref 20), (b) 1-nonanol (ref 24), (c) 1-decanol (ref 24), (d) 1-undecanol. Points, experimental results; solid line, ERAS prediction; dotted line, FBT results; dashed lines, modified UNIFAC (MU) prediction.

Table 7. Correlation of the (Solid + Liquid) and (Liquid + Liquid) Equilibrium Data by Means of the NRTL Equation; Parameters $g_{12} - g_{22}/g_{21} - g_{11}$ and Measures of the Deviations σ_T and σ_x

system	$\frac{g_{12} - g_{22}}{\text{J·mol}^{-1}}$	$\frac{g_{21} - g_{11}}{\text{J·mol}^{-1}}$	α	$\frac{\sigma_T}{\text{K}}$	σ_x
1-octanol (1) + acetonitrile (2)	4513.26	7406.46	0.46	0.64	0.0183
1-nonanol (1) + acetonitrile (2)	3237.66	7368.03	0.41	0.40	0.0127
1-decanol (1) + acetonitrile (2)	5307.19	7981.71	0.43	1.00	0.0086
1-undecanol (1) + acetonitrile (2)	3495.28	8261.74	0.44	0.46	0.0119

may be expressed in a very general manner by eq 11:

$$-\ln x_1 = \frac{\Delta_{\text{fus}}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{\text{fus},1}}\right)+\frac{\Delta_{\text{tr}}H_1}{R}\left(\frac{1}{T}-\frac{1}{T_{\text{tr},1}}\right)-\frac{\Delta_{\text{fus}}C_{\text{p},1}}{R}\left(\ln\frac{T}{T_{\text{fus},1}}+\frac{T_{\text{fus},1}}{T}\right)+\ln\gamma_1 \quad (11)$$

where x_1, γ_1, $\Delta_{\text{fus}}H_1$, $\Delta_{\text{fus}}C_{\text{p},1}$, $T_{\text{fus},1}$, T, ΔH_{tr1}, and $T_{\text{tr},1}$ stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute (here 1-alkanol) heat capacity between the liquid and solid phase at melting temperature, melting temperature, equilibrium temperature, enthalpy of the solid−solid-phase transition, and transition temperature, respectively. If a solid−solid-phase transition occurs before fusion, the solubility equation for temperatures below that of the phase transition must include the effect of the transition. The existence of the solid−solid-phase transition was observed for 1-undecanol and was described previously.[4] For the other 1-alkanols, $\Delta_{\text{tr}}H_1 = 0$, and eq 11 has to be used without this term. The thermophysical data of the pure compounds are presented in Table 1.

The parameters of the equations were fund by an optimization technique using Marquardt's or Rosenbrock's maximum likelihood method of minimalization:

$$\Omega = \sum_{i=1}^{n} [(T_i)^{\text{exp}} - (T_i(x_{1i}P_1, P_2))^{\text{cal}}]^2 \quad (12)$$

where Ω is the objective function; n is the number of

Table 8. Correlation of the (Solid + Liquid) Data of the 1-Alkanol + Nitrile Mixtures by Means of the NRTL 1, Wilson, and UNIQUAC ASM Equations: Values of Parameters and Measures of Deviations

	parameters			deviations		
	NRTL1[a]	Wilson	UNIQAC ASM	NRTL1[b]	Wilson[b]	UNIQAC ASM[b]
	$g_{12} - g_{22}$ $g_{21} - g_{11}$	$\lambda_{12} - \lambda_{22}$ $\lambda_{12} - \lambda_{22}$	$u_{12} - u_{22}$ $u_{21} - u_{11}$	σ_T	σ_T	σ_T
system	J·mol^{-1}	J·mol^{-1}	J·mol^{-1}	K	K	K
			1-Alkanol (1) + Propanenitrile (2)			
1-octanol	4069.27	3590.98	3804.72	0.47	0.49	1.66
	3432.58	5132.90	−899.05			
1-nonanol	3923.20	4250.20	3692.40	0.87	0.60	1.95
	4006.55	4855.41	−876.44			
1-decanol	4394.77	4558.14	4010.92	0.82	0.28	1.56
	4441.93	5543.20	−915.44			
1-undecanol	4123.23	3827.96		0.62	0.40	
	3754.91	4953.20				
			1-Alkanol (1) + Butanenitrile (2)			
1-octanol	3798.97	3372.00	3589.33	0.31	0.25	2.40
	3913.12	3677.77	−1215.15			
1-nonanol	3835.76	3107.82	3768.31	0.92	0.77	3.38
	3746.07	3845.39	−1282.62			
1-decanol	4359.46	3072.40	3906.81	0.50	0.61	1.77
	4011.87	4343.97	−1274.63			
1-undecanol	3632.28	2557.43	3695.72	0.33	0.34	2.21
	3256.81	3777.13	−1345.56			

[a] Calculated with the third nonrandomness parameter α = 0.4 for (1-alkanol + propanenitrile) mixtures and α = 0.5 for (1-alkanol + butanenitrile) mixtures. [b] According to eq 13 in the text.

experimental points; $(T_i)^{\text{exp}}$ and $(T_i)^{\text{cal}}$, respectively, are the experimental and calculated equilibrium temperatures corresponding to the concentration x_{1i}; P_1 and P_2 are the model parameters resulting from the minimization procedure. The root-mean-square deviation of temperature was used as a measure of the goodness of the solubility correlation:

$$\sigma_T = \left(\sum_{n}^{i=1} \frac{((T_i)^{\text{exp}} - (T_i)^{\text{cal}})^2}{n - 2}\right)^{1/2} \tag{13}$$

where n is the number of experimental points.

The pure-component structural parameters r (volume parameter) and q (surface parameter) in the UNIQUAC ASM and NRTL1 equations were obtained by means of the following simple relationships:

$$r_i = 0.02981 V_m \tag{14}$$

$$q_i = \frac{(Z - 2)r_i}{Z} + 1\,\frac{2(1 - l_i)}{Z} \tag{15}$$

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 linear molecules. Table 8 lists the results of fitting the solubility curves by the three equations used: NRTL1, UNIQUAC ASM, and Wilson. Positive deviations from ideality were found for all mixtures, thus the solubility is lower than the ideal one, $\gamma_1 > 1$. The values of activity coefficients in the systems (1-alkanol + propanenitrile or butanenitrile) at low mole fraction of 1-alkanol were from 15 to 25.

ERAS Model. The ERAS model[26,28,50] combines the real associated solution model with a free volume contribution using Flory's equation of state.[31,51] A special property of the ERAS theory is its ability to predict simultaneously V_m^E and H_m^E of mixtures with self- and cross-associations. The version of the ERAS model, related to mixtures consisting of one associating component (1-alkanol) and intermolecular association 1-alkanol-nitrile, has been used to describe the experimental V_m^E and H_m^E data (taken from literature[20,24] and our data) for the mixtures propanenitrile and butanenitrile with 1-alkanols. The equations obtained for the thermodynamic excess functions are split into two additive terms, which arise from the hydrogen bonding effects (so-called "chemical" contribution), and from nonpolar van der Waals interactions, which accounts for the free volume effects between unlike molecules (the "physical" contribution). The interaction parameter χ_{AB} is the only adjustable parameter of the physical part of V_m^E and H_m^E.[39,52] The remaining K_{AB}, Δh^*_{AB}, Δv^*_{AB}, and χ_{AB} are usually simultaneously adjusted to V_m^E and H_m^E experimental data. More details are given in the literature.[39,26,52] Parameters for pure compounds analyzed in this work are listed in Table 9. The ERAS parameters for 1-alkanol + nitrile interactions are presented in Table 10.

Table 9. Characteristic Parameters of Pure Components at 298.15 K Needed for ERAS and FBT Models

	α	κ_T	Δh^*	Δv^*	
component	10^{-4} K^{-1}	10^{-7} kPa^{-1}	kJ·mol^{-1}	cm^3·mol^{-1}	K_A
1-octanol	8.27[a]	7.77[b]	−21.9[c]	−5.6[d]	98[b]
1-nonanol	8.18[e]	7.40[e]	−21.9[c]	−5.6[d]	91.85[f]
1-decanol	8.12[a]	7.33[b]	−21.8[c]	−5.6[d]	88[b]
1-undecanol	8.06[e]	7.34[e]	−21.8[g]	−5.6[d]	82.2[f]
propanenitrile	12.63[h]	10.26[h]			
butanenitrile	11.58[i]	9.81[j]			

[a] Ref 53. [b] Ref 28. [c] Recalculated for 298.15 K from ref 54. [d] Ref 39. [e] Ref 32. [f] Values interpolated or extrapolated for alkanols from C_3 to C_{16}, according to ref 54. [g] Ref 55. [h] Values interpolated according to refs 25 and 56. [i] Ref 25. [j] Ref 57.

Flory−Benson−Treszczanowicz Model. The FBT model has been applied first to the excess volumes of binary systems formed by mixing a polar substance base with an alkane or cycloalkanes.[32,33] The excess volumes are described as the sum of two contributions. One arises from self-association of an 1-alkanol base and is evaluated according to the Mecke−Kempter continuous association model.[30] Application of the Flory theory requires equation

Table 10. ERAS Model Parameters for Binary Mixtures at 298.15 K

mixture	K_{AB}	Δh^* / $kJ \cdot mol^{-1}$	Δv^* / $cm^3 \cdot mol^{-1}$	χ_{AB} / $J \cdot cm^{-3}$
1-octanol + propanenitrile	1.0	51	−10.5	1
1-nonanol + propanenitrile	0.9	53	−10.5	6
1-decanol + propanenitrile	0.8	62	−10.5	7
1-undecanol + propanenitrile	0.8	62	−10.5	8
1-octanol + butanenitrile	0.9	50	−10.5	4
1-nonanol + butanenitrile	0.8	52	−10.5	8.5
1-decanol + butanenitrile	0.7	60	−10.5	10
1-undecanol + butanenitrile	0.7	60	−10.5	12

Table 11. FBT Model Parameter for Binary Mixtures at 298.15 K

system	χ_{AB} / $J \cdot cm^{-3}$
1-octanol + propanenitrile	−2.8
1-nonanol + propanenitrile	2.3
1-decanol + propanenitrile	3.7
1-undecanol + propanenitrile	4.5
1-octanol + butanenitrile	1.2
1-nonanol + butanenitrile	5.5
1-decanol + butanenitrile	7.6
1-undecanol + butanenitrile	9.9

of state parameters for the pure components. The pure component parameters needed for calculations were used from literature sources as given in Table 9. The FBT parameters for 1-alkanol + nitrile interactions are presented in Table 11.

Modified UNIFAC (Dortmund Version). Modified UNIFAC (MU)[34] differs from the original UNIFAC[58] by combinatorial term and the temperature dependence of the group interaction parameters. The corresponding published geometrical and interaction parameters were used without modification.[34] Equations were given in ref 59.

In the MU model, alkanols are characterized by two main groups, OH and CH_3OH. The former is subdivided in the subgroups OH(p), OH(s), and OH(t), which represent the hydroxyl group in primary, secondary, and tertiary alkanols. Nitriles are characterized by the main group CH_3-CN, which is subdivided in subgroup CH_2CN. The subgroups have different geometrical parameters, but the subgroups within the same main group are assumed to have identical group energy−interaction parameters. The interaction parameters were taken from the literature.[34]

Conclusions

The results presented in this paper indicate that the solubilities and excess functions of (1-alkanol + nitrile) systems are controlled by interactions that are weaker than those found in (1-alkanol + amine) mixtures. The competition between hydrogen bonded 1-alkanol molecules and the unlike molecules association is an important factor determining the phase behavior. The known specific interaction of the nitrogen atoms of nitrile with hydroxyl group is stronger for the propanenitrile and butanenitrile than for acetonitrile, because no miscibility gap in the liquid phase was observed.

The results obtained from our study reveal that positive values of V_m^E and H_m^E, observed for (1-alkanol + nitrile) mixtures, were confirmed by the phase diagrams. Contrary to (1-alkanol + an amine) mixtures with strong negative excess functions, the congruently melting addition compounds were not observed.[1−4] The excess molar volumes for mixtures of 1-octanol with acetonitrile[6,13] or of 1-decanol with acetonitrile[60] have very similar values for those of with 1-decanol with propanenitrile (this work) and butanenitrile.[24] More important, the excess molar enthalpies for 1-alkanols under study with acetonitrile mixtures were never measured. From the solid−liquid and liquid−liquid phase diagrams we can conclude that the H_m^E values for (1-alkanol + acetonitrile) mixtures will be higher (weaker unlike molecules interaction) than presented here for propanenitrile and butanenitrile.

Finally, it should be noted that modeling of the experimental excess functions is better with the ERAS model than with the MU model and can describe simultaneously V_m^E and H_m^E values (see Figures 6−8). The MU model well predicts the solid−liquid equilibrium curves and overestimates the liquid−liquid equilibrium curves. DISQUAC[61] interaction parameters are not available yet.

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Received for review July 7, 2005. Accepted July 31, 2005. We gratefully acknowledge the Warsaw University of Technology for financial support.

JE050262M