JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

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Measurements, Correlations, and Mod. UNIFAC (Do) Prediction of (Solid−Liquid) Phase Equilibria Diagrams in Binary Systems (Aliphatic Ketone + an Alcohol)

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S *Supporting Information*

ABSTRACT: The (solid−liquid) phase equilibria (SLE) of binary mixtures containing fragrance raw materials {heptan-2-one, or nonan-2-one, or undecan-2-one, or dodecan-2-one, or tridecan-2-one + octan-1-ol, or decan-1-ol, or dodecan-1-ol} were investigated. These systems have been measured by a dynamic method over a wide temperature range from (230 to 300) K and ambient pressure. All binary systems revealed simple eutectic mixtures with complete miscibility in the liquid phase. The experimental data were correlated by the UNIQUAC, NRTL, and Wilson equations, utilizing parameters derived from the SLE. The standard deviations of the solubility temperatures were (0.52, 0.52, and 0.46) K for the UNIQUAC, NRTL, and Wilson equations, respectively. The Mod. UNIFAC (Do) representation of the SLE with known, literature parameters has given very good results.

INTRODUCTION

The technological processes of organic liquid mixtures containing fragrance raw materials (FRM) such as aliphatic ketones and alcohols need important information involving the mutual solubilities. FRM are used in a variety of consumer products ranging from food to cosmetics such as creams, lotions, detergents, and various other personal and household products. The potential for exposure to these materials in our society is, therefore, very high, particularly for those products that come into direct contact with the skin. The safety evaluation of flavors and a large number of diverse chemicals used as fragrance ingredients has recently been published.[1−3] The hundreds of substances—acids, esters, ketones, ethers, and alcohols—as FRM have been accepted as "generally recognized as safe substances", and some have become the leading preservatives for food as well as for pharmaceutical and cosmetic preparations.[4,5]

The ketones used as a FRM can be found in nature in coffee, fruits, different kinds of cheese, cognac, guava, kiwi, some south European trees, secretion of ants, tobacco, beef, and meat of goats.[6−17] In nature, heptan-2-one exists in beef,[6] in meat of goats (together with nonan-2-one and undecan-2-one),[7] in blue cheese (produced by the *Penicillium roqueforti*),[7] in blue cheese Stilton (together with nonan-2-one),[8] in cheese Camembert (produced by the *Penicillium caseifulvum*, *Penicilliumin camemberti*) (together with nonan-2-one and undecan-2-one),[9] in chocolate,[10] in tobacco,[11] and in coffee[12] (together with nonan-2-one). The longer chain ketones such as undecan-2-one and tridecan-2-one are the odor and/or flavor in gouda cheese,[13] in alcohols Calvados and Cognac,[14] and in Chinese vodka Moutai.[11] The tridecan-2-one exists in melting cheese.[15] Natural tridecan-2-one is in the secretion of ants.[16]

Popular raw materials such as nonan-2-one, benzothiazole, nonanal, and 4-carvomenthenol are used as flavor compositions in new cloths.[17]

During the past few years, we have focused on the determination of (solid−liquid) phase equilibria of FRM based on 2,3-pentanedione[18] and cyclohexane with alcohols at ambient and high pressure.[19,20]

This work includes the phase equilibria measurements of FRMs: {heptan-2-one, or nonan-2-one, or undecan-2-one, or dodecan-2-one, or tridecan-2-one + octan-1-ol, or decan-1-ol, or dodecan-1-ol} at temperatures from (230 to 300) K and ambient pressure. In this work the hydrogen bonding may be expected between the carbonyl group of all ketones and the hydroxyl group of alcohols.

EXPERIMENTAL SECTION

Materials. Investigated compounds were: heptan-2-one (CAS No. 110-43-0), nonan-2-one (CAS No. 821-55-6), undecan-2-one (CAS No. 112-12-9), dodecan-2-one (CAS No. 6175-49-1), and tridecan-2-one (CAS No. 593-08-8). These substances and alcohols were purchased from Sigma-Aldrich Chemie GmbH, Stenheim, Germany. The purity of compounds was ≥ 0.99 mass fractions. Ketones were used without any purification.

Before use, alcohols were purified by fractional distillation (octan-1-ol and decan-1-ol) and crystallization (dodecan-1-ol) to the mass fraction purity ≥ 0.998. All compounds were checked by gas−liquid chromatography (GLC) analysis, and no significant impurities were found.

Differential Scanning Microcalorimetry (DSC). Basic thermal characteristics of ketones, i.e., temperature of fusion ($T_{\mathrm{fus},1}$) and enthalpy of fusion ($\Delta_{\mathrm{fus}}H_1$), have been measured using a differential scanning microcalorimetry technique (DSC). The applied scan rate was 5 $\mathrm{K \cdot min^{-1}}$, with a power and recorder sensitivity of 16 $\mathrm{mJ \cdot s^{-1}}$ and 5 mV, respectively.

Special Issue: John M. Prausnitz Festschrift

Received: July 9, 2010
Accepted: September 4, 2010
Published: October 05, 2010

dx.doi.org/10.1021/je100725a | J. Chem. Eng. Data 2011, 56, 881–888

Table 1. Thermophysical Constants of Pure Substances, Melting Temperature, T_{fus} (Experimental and Literature Values), Enthalpy of Fusion, $\Delta_{\mathrm{fus}}H$ (Experimental and Literature Values), and Change of Heat Capacity at Melting Temperature, $\Delta_{\mathrm{fus}}C_p$, as Determined From Differential Scanning Calorimetry Data

	T_{fus} (exptl)	T_{fus} (lit.)	$\Delta_{\mathrm{fus}}H$(exptl)	$\Delta_{\mathrm{fus}}H$(lit.)	$\Delta_{\mathrm{fus}}C_p$(lit.)
compounds	K	K	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
heptan-2-one	237.0[a] 236.5[b]	237.65[c] 238[e]	19.089[b]	19.71[c] 18.4[d] 19.71[e]	
nonan-2-one	263.4[a] 263.68[b]	265.65[e]	27.347[b]	25.6[d] 26.865[e]	
undecan-2-one	284.8[a] 285.26[b]	285.9[e]	36.344[b]	33.56[e]	
dodecan-2-one	294.0[a] 294.27[b]	293.65[e]	39.480[b]	36.966[e]	
tridecan-2-one	300.8[a] 301.75[b]	300.65[e]	44.030[b]	40.333[e]	
octan-1-ol	258.6[a]	257.65[e]	23.700[b]	23.70[f] 22.6[d]	41.33[g]
decan-1-ol	279.5[a]	280.05[e]	31.400[b]	28.79[f] 31.2[d] 37.66[e]	82.65[h]
dodecan-1-ol	296.6[a]	296.95[e]	37.740[b]	38.42[f] 40.2[d] 40.2[d]	139.30[i]

[a] From the SLE measurements. [b] This work by DSC. [c] From ref 21. [d] From ref 22. [e] From ref 23. [f] From ref 24. [g] From ref 25. [h] From ref 26. [i] From ref 27.

The apparatus (Perkin-Elmer Pyris 1) was calibrated with a 0.999999 mol fraction purity indium sample. The repeatability of the melting temperature measurements was ± 0.05 K. The repeatability of the measured enthalpy of fusion was $\Delta_{\mathrm{fus}}H_1 = \pm\ 5\ \mathrm{J \cdot mol^{-1}}$. The DSC thermographs are shown in Figures 1S to 5S in the Supporting Information. The thermophysical characterization of the compounds is presented in Table 1.

(Solid−Liquid) Phase Equilibria Apparatus and Measurements. Solid solubilities have been determined using a dynamic (synthetic) method described previously.[28] Mixtures of solute and solvent were prepared by weighing the pure components to within $1 \cdot 10^{-4}$ g. The sample of solute and solvent was heated very slowly (at less than 2 $\mathrm{K \cdot h^{-1}}$ 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 a calibrated Gallenkamp Autotherm II thermometer totally immersed in the thermostatting liquid. The measurements were carried out over the whole mole fraction range from 0 to 1. Mixtures were prepared by weighing the pure compounds with an uncertainty of $1 \cdot 10^{-4}$ g, and errors did not exceed $2 \cdot 10^{-4}$ in mole fraction. The uncertainties of the temperature measurements were judged to be 0.1 K. The repeatability of the SLE experimental point was ± 0.1 K.

■ RESULTS AND DISCUSSION

The experimental data of (solid−liquid) phase equilibria of 15 binary systems are listed in Tables 2 to 6. The tables include the direct experimental results of the SLE: equilibrium temperatures in the saturated solution, T/K versus x_1, the mole fraction of the ketone.

Table 2. Experimental Results of (Solid−Liquid) Phase Equilibrium in Binary Systems {Heptan-2-one (1) + an Alcohol (2)}: Equilibrium Composition, x_1, and Temperature, T

Octan-1-ol		Decan-1-ol		Dodecan-1-ol	
x_1	T/K	x_1	T/K	x_1	T/K
1.0000	237.0	1.0000	237.0	1.0000	237.0
0.9473	235.7	0.9939	237.0	0.9857	246.4
0.9022	235.0	0.9928	239.3	0.9494	263.0
0.8545	237.1	0.9833	241.1	0.8950	270.9
0.8319	239.0	0.9398	247.2	0.8507	275.8
0.8053	240.5	0.8954	254.1	0.7981	278.8
0.7582	242.9	0.8460	258.7	0.7481	281.1
0.7074	244.6	0.7969	262.0	0.6506	284.4
0.6580	246.4	0.7518	263.8	0.6026	285.6
0.6086	247.5	0.7012	265.8	0.5571	286.7
0.5590	249.0	0.6494	267.3	0.5010	287.6
0.4986	249.9	0.6004	268.7	0.4529	288.8
0.4495	251.0	0.5497	269.8	0.4040	289.8
0.3994	251.4	0.4988	270.9	0.3425	291.0
0.3500	252.6	0.4475	272.1	0.2816	292.0
0.2981	253.6	0.3869	273.4	0.2177	293.3
0.2071	255.3	0.3214	274.5	0.1605	294.4
0.1355	256.7	0.2749	275.4	0.0774	295.7
0.0522	258.2	0.2235	276.4	0.0000	296.6
0.0000	258.6	0.1601	277.7		
		0.1017	278.0		
		0.0000	279.5		

Table 3. Experimental Results of (Solid−Liquid) Phase Equilibrium in Binary Systems {Nonan-2-one (1) + an Alcohol (2)}: Equilibrium Composition, x_1, and Temperature, T

Octan-1-ol		Decan-1-ol		Dodecan-1-ol	
x_1	T/K	x_1	T/K	x_1	T/K
1.0000	263.4	1.0000	263.4	1.0000	263.4
0.9524	262.7	0.9393	262.9	0.9746	263.6
0.9174	261.9	0.8884	261.9	0.9337	267.4
0.8463	261.2	0.8349	260.7	0.8789	272.2
0.7906	260.2	0.7819	261.5	0.8060	277.2
0.7454	259.8	0.7341	263.6	0.7363	280.6
0.6929	258.9	0.6647	266.0	0.6678	283.1
0.6452	258.3	0.5888	267.9	0.5816	285.9
0.5959	257.7	0.5115	269.6	0.4854	287.6
0.5440	257.0	0.4472	271.1	0.4143	289.5
0.5009	256.3	0.3782	272.6	0.3381	290.8
0.4627	255.6	0.2990	274.1	0.2600	292.7
0.4220	254.9	0.2182	275.7	0.1791	294.0
0.3780	254.6	0.1511	277.2	0.1014	295.4
0.3388	253.7	0.0928	278.2	0.0000	296.6
0.2966	253.5	0.0000	279.5		
0.2557	254.4				
0.2175	256.1				
0.2002	255.6				
0.1598	256.2				
0.1075	256.9				
0.0862	258.4				
0.0831	257.2				
0.0000	258.6				

7Experimental phase diagrams of SLE at ambient pressure, investigated in this work, are shown in Figures 1 to 7. These mixtures present simple eutectic systems with complete miscibility in the liquid phase. The liquidus curves depend on the melting temperature of two compounds. The solubility of all ketones in alcohols decreases as the melting temperature and the chain length of an alcohol increases. The eutectic points for heptan-2-one, nonan-2-one, undecan-2-one, dodecan-2-one, and tridecan-2-one in the mixture with the certain alcohol shift toward the lower ketone mole fraction. The eutectic temperatures of the systems {ketone (1) + an alcohol (2)} increase with an increase of an alcohol chain length.

Similar results were observed in our earlier work for binary systems of 2,3-pentanedione (additive of butter) with alcohols (hexadecan-1-ol, or octadecan-1-ol, or eicosan-1-ol)[18] and in cyclohexane-based compounds with alcohols (octan-1-ol, decan-1-ol, and dodecan-1-ol).[19,20]

The carbonyl group of ketone and the hydroxyl group of alcohols are responsible for the strong interaction between dissimilar molecules in the liquid phase and complete miscibility in the liquid phase.

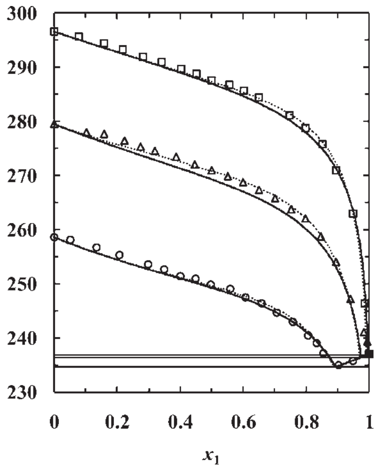

Figure 1. Solid−liquid equilibria in binary systems {heptan-2-one (1) + an alcohol (2)}: ○, octan-1-ol; △, decan-1-ol; □, dodecan-1-ol. Dotted lines were designated by the UNIQUAC equation with parameters given in Table 2. Solid lines represent Mod. UNIFAC (Do) predictions.

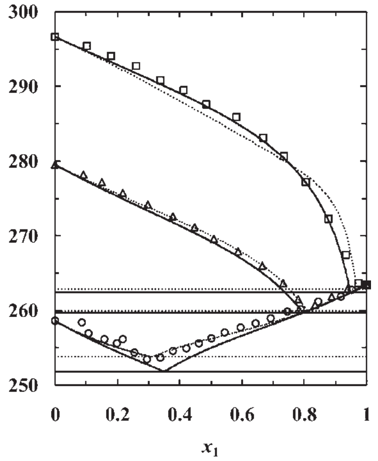

Figure 2. Solid−liquid equilibria in binary systems {nonan-2-one (1) + an alcohol (2)}: ○, octan-1-ol; △, decan-1-ol; □, dodecan-1-ol. Dotted lines were designated by the UNIQUAC equation with parameters given in Table 2. Solid lines represent Mod. UNIFAC (Do) predictions.

■ MODELING SECTION

For the (solid−liquid) phase equilibrium in the binary system with the pure solid phase composed of component 'i' and the saturated solution of 'i' as the second phase, one can derive the following relation between mole fraction of component 'i' (x_i) and temperature (T)

$$\ln x_i = -\frac{\Delta_{\text{fus}}H_i}{RT}\left(1-\frac{T}{T_{\text{fus},i}}\right) + \frac{\Delta_{\text{fus}}C_{p,i}}{R}\left(\ln\frac{T}{T_{\text{fus},i}}+\frac{T_{\text{fus},i}}{T}-1\right) - \ln\gamma_i(x_1, T, \mathbf{a}) \quad (1)$$

where i = 1, 2 and $x_1 + x_2 = 1$. In the above equation, the $T_{\text{fus},i}$ stands for normal temperature of fusion, $\Delta_{\text{fus}}H_i$ for enthalpy of fusion, and $\Delta_{\text{fus}}C_{p,i}$ for heat capacity change at $T_{\text{fus},i}$ for pure component 'i'. The activity coefficient of solute 'i' in the liquid phase, γ_i, depends on x_i, T, and some parameters $\mathbf{a}$ provided by a

Table 4. Experimental Results of (Solid−Liquid) Phase Equilibrium in Binary Systems {Undecan-2-one (1) + an Alcohol (2)}: Equilibrium Composition, x_1, and Temperature, T

Octan-1-ol		Decan-1-ol		Dodecan-1-ol	
x_1	T/K	x_1	T/K	x_1	T/K
1.0000	284.8	1.0000	284.8	1.0000	284.8
0.9548	284.5	0.9455	284.7	0.9818	283.8
0.8958	283.7	0.8944	284.0	0.9304	283.1
0.8473	282.9	0.8495	283.4	0.8822	282.4
0.8005	282.3	0.7982	282.5	0.8354	281.8
0.7516	281.7	0.7469	281.8	0.7859	281.2
0.7027	281.0	0.6763	281.0	0.7328	281.6
0.6495	280.3	0.6434	280.4	0.6938	282.7
0.6005	279.6	0.6060	279.8	0.6531	284.1
0.5345	278.9	0.5723	279.3	0.6160	285.3
0.5179	278.4	0.5265	278.6	0.5686	286.6
0.4772	277.7	0.4871	277.5	0.5181	287.5
0.4282	276.8	0.4486	277.0	0.4684	288.7
0.3789	275.7	0.4223	276.1	0.4184	289.6
0.3276	274.3	0.3872	276.0	0.3689	290.5
0.2891	273.3	0.3709	274.7	0.3285	291.2
0.2491	271.7	0.3582	276.0	0.2610	292.6
0.1845	268.4	0.3407	273.7	0.2037	293.5
0.1531	266.9	0.3345	274.3	0.1464	293.8
0.1157	263.9	0.3109	274.0	0.0889	294.6
0.0000	258.6	0.2699	274.7	0.0426	295.5
		0.2313	275.4	0.0000	296.6
		0.1915	276.3		
		0.1466	277.0		
		0.0993	277.7		
		0.0506	278.6		
		0.0000	279.5		

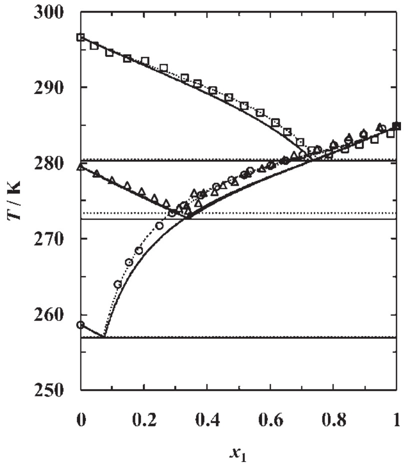

Figure 3. Solid−liquid equilibria in binary systems {undecan-2-one (1) + an alcohol (2)}: ○, octan-1-ol; △, decan-1-ol; □, dodecan-1-ol. Dotted lines were designated by the UNIQUAC equation with parameters given in Table 2. Solid lines represent Mod. UNIFAC (Do) predictions.

theoretical model. By fixing the composition x_i and model (thus a) in eq 1, one can calculate equilibrium temperature T.

Table 5. Experimental Results of (Solid−Liquid) Phase Equilibrium in Binary Systems {Dodecan-2-one (1) + an Alcohol (2)}: Equilibrium Composition, x_1, and Temperature, T

Octan-1-ol		Decan-1-ol		Dodecan-1-ol	
x_1	T/K	x_1	T/K	x_1	T/K
1.0000	294.0	1.0000	294.0	1.0000	294.0
0.9386	293.0	0.9438	292.4	0.9384	292.2
0.8957	292.2	0.8951	291.5	0.8974	291.4
0.8498	291.4	0.8361	290.6	0.8467	290.6
0.8044	290.7	0.7845	289.9	0.7913	289.8
0.7553	289.9	0.7239	289.0	0.7453	289.1
0.6893	289.1	0.6601	288.2	0.6916	288.4
0.6402	288.3	0.5979	287.4	0.6313	287.5
0.6001	287.7	0.5382	286.3	0.5993	286.6
0.5369	286.9	0.4751	285.2	0.5791	286.0
0.4857	285.8	0.4165	283.9	0.5773	286.2
0.4367	285.0	0.3660	282.7	0.5327	286.7
0.3867	283.8	0.3070	281.0	0.4935	286.8
0.3266	282.3	0.2677	279.9	0.4678	287.3
0.2666	280.5	0.2321	278.4	0.4430	288.5
0.1828	277.1	0.2096	277.6	0.3982	288.5
0.1386	274.1	0.1781	277.2	0.3897	289.0
0.0803	268.5	0.1409	278.3	0.3270	289.7
0.0334	264.3	0.0687	279.4	0.2719	291.3
0.0596	256.3	0.0000	279.5	0.2100	292.3
0.0000	258.6			0.1557	293.2
				0.1032	294.1
				0.0430	295.1
				0.0000	296.6

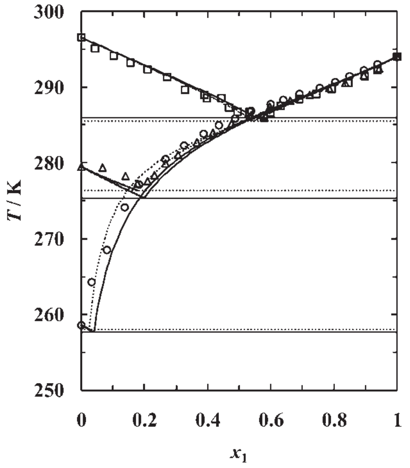

Figure 4. Solid−liquid equilibria in binary systems {dodecan-2-one (1) + an alcohol (2)}: ○, octan-1-ol; △, decan-1-ol; □, dodecan-1-ol. Dotted lines were designated by the UNIQUAC equation with parameters given in Table 2. Solid lines represent Mod. UNIFAC (Do) predictions.

Activity coefficients required for the SLE calculations can be described in terms of many different models. In this work, we performed experimental data correlation by using UNIQUAC,[29] NRTL,[30] and Wilson equations.[31] By minimization of the

Table 6. Experimental Results of (Solid−Liquid) Phase Equilibrium in Binary Systems {Tridecan-2-one (1) + an Alcohol (2)}: Equilibrium Composition, x_1, and Temperature, T

Octan-1-ol		Decan-1-ol		Dodecan-1-ol	
x_1	T/K	x_1	T/K	x_1	T/K
1.0000	300.8	1.0000	300.8	1.0000	300.8
0.9650	300.3	0.9398	300.5	0.9488	299.8
0.9196	299.5	0.8976	299.6	0.8923	298.7
0.8746	298.6	0.8560	298.6	0.8559	297.9
0.8187	298.1	0.8057	297.8	0.8051	297.3
0.7686	297.6	0.7583	297.3	0.7541	296.8
0.7185	296.8	0.7084	296.5	0.7020	296.0
0.6250	294.8	0.6587	295.8	0.6605	295.2
0.5885	294.2	0.6092	295.3	0.6133	294.4
0.5329	293.6	0.5723	294.4	0.5659	293.5
0.4782	292.8	0.5217	293.8	0.5167	292.7
0.4146	291.9	0.4771	293.0	0.4666	291.6
0.3681	290.2	0.4297	291.9	0.4203	290.4
0.3214	288.9	0.3914	291.4	0.4014	290.0
0.2452	287.3	0.3416	290.4	0.3819	289.5
0.2070	285.0	0.3200	288.7	0.3705	289.9
0.1577	282.6	0.2953	287.5	0.3608	289.8
0.1292	280.7	0.2614	286.5	0.3355	290.3
0.0918	278.6	0.2051	284.3	0.3217	290.8
0.0422	270.0	0.1564	281.4	0.2904	291.1
0.0124	263.3	0.1061	279.2	0.2852	290.8
0.0000	258.6	0.0661	278.9	0.2349	291.6
		0.0648	279.2	0.2128	291.9
		0.0408	279.1	0.1733	293.6
		0.0220	279.3	0.1344	294.1
		0.0000	279.5	0.0762	295.4
				0.0399	296.1
				0.0000	296.6

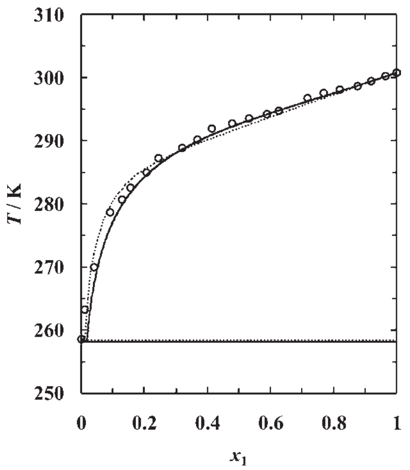

Figure 5. Solid−liquid equilibria in binary systems {tridecan-2-one (1) + octan-1-ol (2)}: ○, experimental data. Dotted line was designated by the UNIQUAC equation with parameters given in Table 2. Solid line represents Mod. UNIFAC (Do) prediction.

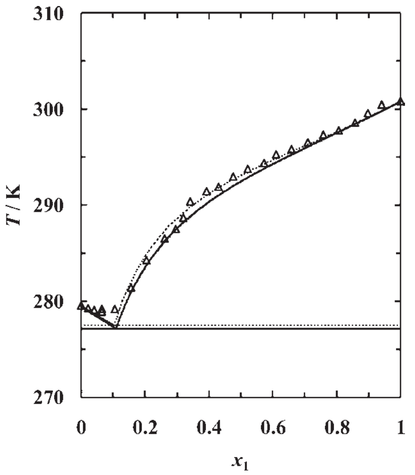

Figure 6. Solid−liquid equilibria in binary systems {tridecan-2-one (1) + decan-1-ol (2)}: △, experimental data. Dotted line was designated by the UNIQUAC equation with parameters given in Table 2. Solid lines represent Mod. UNIFAC (Do) prediction.

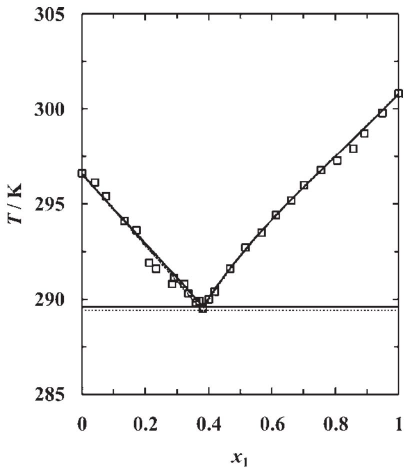

Figure 7. Solid−liquid equilibria in binary systems {tridecan-2-one (1) + dodecan-1-ol (2)}: □, experimental data. Dotted line was designated by the UNIQUAC equation with parameters given in Table 2. Solid lines represent Mod. UNIFAC (Do) prediction.

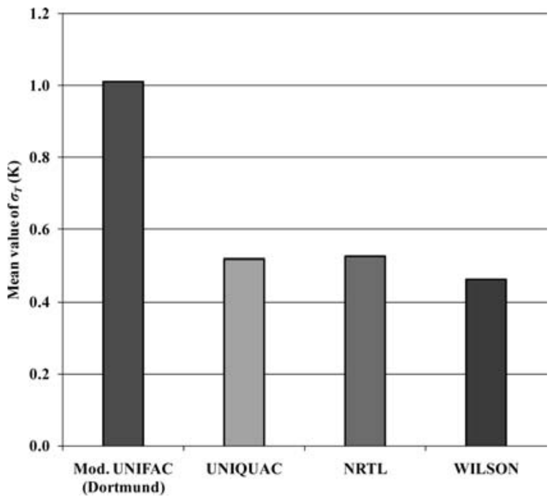

Figure 8. Comparison of mean values of standard deviations of (solid−liquid) equilibrium temperature for different models: UNIQUAC, NRTL, and Wilson equations (correlation) and Mod. UNIFAC (Do) (prediction).

Table 7. Correlation of the (Solid−Liquid) Phase Equilibrium Data of the {Ketone (1) + an Alcohol (2)} Binary Mixtures by Means of the UNIQUAC, NRTL, and Wilson Equations: Values of Parameters and Measures of Deviation

		UNIQUAC			NRTL[b]			Wilson[c]		
		Δu_{12}	Δu_{21}	σ_T[a]	Δg_{12}	Δg_{21}	σ_T[a]	$\Delta\lambda_{12}$	$\Delta\lambda_{21}$	σ_T[a]
		$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	K
heptan-2-one	octan-1-ol	359.06	387.87	0.58	1953.6	891.16	0.58	1592.0	1716.5	0.51
	decan-1-ol	−135.08	849.66	0.45	1773.4	1192.3	0.58	2050.0	924.57	0.40
	dodecan-1-ol	62.381	592.55	0.51	3251.8	−356.32	0.48	1748.5	1328.2	0.44
nonan-2-one	octan-1-ol	294.25	518.82	0.47	975.56	2497.5	0.46	2332.8	1866.0	0.37
	decan-1-ol	352.72	150.47	0.29	1891.2	443.70	0.28	1086.4	1522.4	0.26
	dodecan-1-ol	2074.4	−1013.1	1.50	6979.7	−2415.7	1.56	50.321	4799.1	1.26
undecan-2-one	octan-1-ol	1428.1	−559.31	0.32	2886.0	176.55	0.31	412.95	3016.4	0.26
	decan-1-ol	1501.7	−703.01	0.42	4018.6	−821.41	0.43	247.66	3189.4	0.38
	dodecan-1-ol	−300.84	797.70	0.21	305.02	2097.8	0.20	1903.9	708.90	0.20
dodecan-2-one	octan-1-ol	−22.843	695.04	0.78	−821.92	4328.0	0.76	2476.1	1282.1	0.69
	decan-1-ol	24.820	477.29	0.37	76.524	2568.6	0.36	2060.9	1003.7	0.37
	dodecan-1-ol	123.54	186.05	0.34	838.23	883.75	0.34	940.30	881.75	0.34
tridecan-2-one	octan-1-ol	−310.79	982.45	0.90	−1750.8	5531.2	0.91	2918.8	879.04	0.84
	decan-1-ol	715.66	−217.27	0.46	1139.6	1230.7	0.45	811.65	1803.3	0.44
	dodecan-1-ol	387.41	−67.459	0.18	1075.9	702.81	0.18	679.55	1210.8	0.18

[a] According to eq 3. [b] Nonrandomness parameter: $\alpha_{12} = \alpha_{21} = 0.2$. [c] Molar volumes calculated from densities given in ref 23.

Table 8. Mod. UNIFAC (Do) Group Assignment for the Investigated Ketones and Alcohols

	subgroup symbol (group number; subgroup number)[a]			
	CH_3 (1; 1)	CH_2 (1; 2)	OH(p) (5; 14)	CH_3CO (9; 18)
heptan-2-one	1	4	−	1
nonan-2-one	1	6	−	1
undecan-2-one	1	8	−	1
dodecan-2-one	1	9	−	1
tridecan-2-one	1	10	−	1
octan-1-ol	1	7	1	−
decan-1-ol	1	9	1	−
dodecan-1-ol	1	11	1	−

[a] According to the nomenclature and numbering given in ref 32.

Table 9. Mod. UNIFAC (Do) Structural and Interaction Parameters Used in This Work to Model SLE in Binary Systems (Ketone + an Alkan-1-ol)

	structural parameters[a] (group number; subgroup number)			
	CH_3 (1; 1)	CH_2 (1; 2)	OH(p) (5; 14)	CH_3CO (9; 18)
R_k	0.6325	0.6325	1.2302	1.7048
Q_k	1.0608	0.7081	0.8927	1.6700

		group interaction parameters[b]					
i	j	a_{ij}	b_{ij}	$10^3 c_{ij}$	a_{ji}	b_{ji}	$10^3 c_{ji}$
CH_3	CH_2	−	−	−	−	−	−
CH_3	OH(p)	2777	−4.674	1.551	1606	−4.746	0.9181
CH_3	CH_3CO	433.6	0.1473	0	199	−0.8709	0
CH_2	OH(p)	2777	−4.674	1.551	1606	−4.746	0.9181
CH_2	CH_3CO	433.6	0.1473	0	199	−0.8709	0
OH(p)	CH_3CO	−250	2.857	−6.022	653.3	−1.412	0.9540

[a] From ref 32. [b] UNIFAC Consortium Web site: http://unifac.ddbst.de/.

following objective function

$$F(\mathbf{a}) = \sum_i \{T_i^{\text{calcd}}(\mathbf{a}) - T_i^{\text{exptl}}\}^2 \qquad (2)$$

the model parameters **a** can be obtained. For the calculations, the coded appropriate MATLAB (Mathworks, Inc.) subroutine involving algorithms for solving nonlinear equations as well as the Marquardt nonlinear least-squares procedure was used.

The standard deviation was as follows

$$\sigma_T = \sum_{i=1}^{n} \frac{(T_i^{\text{calcd}} - T_i^{\text{exptl}})}{n} \qquad (3)$$

The correlation was presented with the development of two adjustable parameters. Values of model parameters obtained by fitting solubility curves together with the corresponding standard deviations are given in Table 7. In this work, the value of the parameter α, a constant of proportionality similar to the nonrandomness constant of the NRTL equation, had different values in the calculations for different binary systems (see Table 7). For systems under study, the description of (solid−liquid) phase equilibrium was given by the average standard mean deviation (σ_T) equal to (0.52, 0.52, and 0.46) K for UNIQUAC, Wilson, and NRTL equations, respectively.

The resulting parameters are collected in Table 7, and the correlations using these parameters are presented in Figures 1 to 7. In all systems, the activity coefficients are higher than one ($\gamma_1 > 1$), and the solubility is lower than the ideal solubility.

Activity coefficients can be predicted based only on the molecular structure of the compounds forming a binary mixture, with the group contribution methods (GCMs). Nowadays, the most popular GCM seems to be UNIFAC and its modifications. In the present study, we used a modification of UNIFAC developed by Gmehling et al., the Mod. UNIFAC (Do).[32]

The most important modification compared with the original version of UNIFAC is the temperature dependence of binary group interaction parameters Ψ_{ij}.

To predict SLE diagrams for the presented systems, the decomposition of the studied ketones and alcohols into molecular groups was done. Both the structural and interaction parameters were used for the following Mod. UNIFAC (Do) groups: CH_3, CH_2, CH_3CO, OH(p). For example, in terms of the model, the heptan-2-one molecule is composed as follows: 1 × CH_3, 4 × CH_2, 1 × CH_3CO. Detailed group assignments and binary interactions parameters are given in Tables 8 and 9, respectively. Resulting phase diagrams are shown in Figures 1 to 7. The UNIFAC parameters, known from the literature, describe the (solid−liquid) phase diagrams with low standard deviation, which is presented in comparison with data of correlation of these systems in Figure 8.

■ CONCLUSIONS

New phase equilibrium data on (solid−liquid) of binary mixtures of popular fragrance raw materials with alcohols were presented. These phase diagrams are simple eutectic mixtures with complete miscibility in the liquid phase. The possible hydrogen bonding is responsible for strong interaction in the liquid phase between ketones and alcohols. The solubility decreases as the melting temperature of an alcohol increases. The results of the correlation were obtained with a very low standard deviation and were similar for the three equations used. Surprisingly, the prediction of phase diagrams with Mod. UNIFAC (Do) is extremely good, with standard deviation $\sigma_T \cong 1$ K.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. DSC of all ketones. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

Funding for this research was provided by the Warsaw University of Technology.

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