Solid−Liquid Phase Equilibria of 1-Decanol and 1-Dodecanol with Fragrance Raw Materials Based on Cyclohexane

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The solid−liquid phase equilibria (SLE) of binary mixtures containing 1-decanol or 1-dodecanol and fragrance raw materials based on cyclohexane were investigated. The systems {1-decanol or 1-dodecanol (1) + cyclohexyl carboxylic acid (CCA) or cyclohexyl acetic acid (CAA) or cyclohexyl acetate (CA) or 2-cyclohexyl ethyl acetate (2CEA) or 2-cyclohexyl ethanol (2CE) (2)} have been measured by a dynamic method over a wide range of temperature from (250 to 300) K and ambient pressure. For all systems, SLE diagrams were detected as eutectic mixtures with complete miscibility in the liquid phase. The experimental data were correlated by the Wilson and the nonrandom two-liquid NRTL equation, utilizing parameters derived from the solid−liquid equilibrium. The average root-mean-square deviations of the solubility temperatures were (0.33 and 0.31) K for the Wilson and the NRTL equations, respectively.

Introduction

A list of perfumers, flavors, and a large number of diverse chemicals used as fragrance ingredients and a safety evaluation of these materials has been published.[1−3] The technological processes of organic liquid mixtures containing fragrance compounds including aromatics, aliphatics, and oxygenates with alcohols and water need important information involving the solubilities of fragrance materials (FM). Fragrance materials are used in a variety of consumer products ranging from perfumes to skin products 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 hundreds substances, acids, esters and alcohols, in FM have been "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 esters of cyclohexanol and carboxylic acids used as a FM are formed as byproducts in the process of the commercial oxidation of cyclohexane into cyclohexanone.[6] The data of isobaric heat capacities, densities, speed of sound, enthalpies of vaporization, and enthalpies of phase transitions for ester based on cyclohexanol and carboxylic acids have been published recently.[6,7] Cyclohexyl acetate has also been tested as an entrainer for the solvent extraction and separation of butyric acid from water.[8] There is a pressing need to have more thermodynamic information about solid−liquid equilibria of the FM with solvents as alcohols and water.

Until now, we have focused on the determination of solid−liquid phase equilibria of FM based on cyclohexane with 1-octanol at ambient and high pressure.[9] To the best of our knowledge, the phase equilibria of these substances has not been measured.

This work includes the phase equilibria measurement of FMs, {1-decanol or 1-dodecanol (1) + cyclohexyl carboxylic acid (CCA) or cyclohexyl acetic acid (CAA) or cyclohexyl acetate (CA) or 2-cyclohexyl ethyl acetate (2CEA) or 2-cyclohexyl ethanol (2CE) (2)}, at temperatures from (250 to 300) K and ambient pressure. The chemical names and the abbreviations of substances under study are presented in Table 1. Natural CCA can be found in nature in coffee and as odor, flavor, or both in blueberry, cherry, tropical fruit, pineapple, raisin, and raspberry.[1] CAA is used as an odor, flavor, or both in caramel, chocolate cocoa, coffee, honey, and maple.[1] Natural CA exists in sauerkraut and is used as odor, flavor, or both in apple, banana, blackberry, raspberry, and rum.[1] 2CEA is used as odor, flavor, or both in balsam, floral, raspberry, and rose.[1] 2CE is the most popular raw material and is used as odor, flavor, or both in more than 100 substances, the most important of which are apple green, cognac, guava, kiwi, magnolia, nut, and rose.[1]

In this work, strong interactions may be expected among all FMs possessing different polar groups with 1-alkanols. A higher solubility of FM in a chosen solvent means possible hydrogen bonding and other intermolecular interactions between FM and solvent.

Experimental Section

Materials. Investigated compounds were: cyclohexyl carboxylic acid ($C_7H_{12}O_2$, CCA) (CAS no. 98-89-5), cyclohexyl acetic acid ($C_8H_{14}O_2$, CAA) (CAS no. 5292-21-7), cyclohexyl acetate ($C_8H_{14}O_2$, CA) (CAS no. 622-45-7), 2-cyclohexyl ethyl acetate ($C_{10}H_{18}O_2$, 2CEA) (SAFC Supply Solutions, St. Louis, MO, CAS no. 21722-83-8), and 2-cyclohexyl ethanol ($C_8H_{16}O$, 2CE) (CAS no. 4442-79-9). The substances CCA, CAA, CA, and 2CE and solvents 1-decanol and 1-dodecanol were purchased from Sigma-Aldrich Chemie GmbH, Stenheim, Germany. The purity of compounds was ≥ 0.98 mass fraction. Chemicals were used without any purification.

Before use, solvents were purified by fractional distillation (1-decanol) and crystallization (1-dodecanol) to the mass fraction purity of ≥ 0.998. All compounds were checked by gas−liquid chromatography (GLC) analysis, and no significant impurities were found. The thermophysical characterization of the compounds was obtained by the differential scanning microcalorimetry (DSC) in our previous work.[9]

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Table 1. Structure, Name, Abbreviation of Name, and Values of Molar Mass of the Investigated Compounds

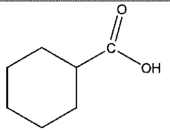
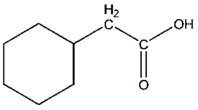
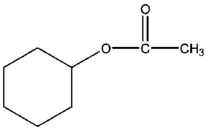
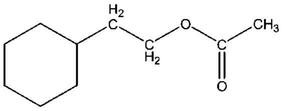
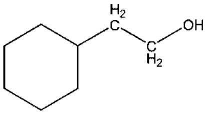
compound	structural formula	abbreviation M/g·mol^{-1}
cyclohexyl carboxylic acid		CCA 128.17
cyclohexyl acetic acid		CAA 142.20
cyclohexyl acetate		CA 142.20
2–cyclohexyl ethyl acetate		2CEA 170.24
2–cyclohexyl ethanol		2CE 128.22

Table 2. Thermophysical Constants of Pure Substances: Melting Temperature, T_{fus}; Enthalpy of Fusion, $\Delta_{fus}H$; Phase Transition Temperature, T_{tr}; Enthalpy of Phase Transition, $\Delta_{tr}H$; Change of Heat Capacity at Melting Temperature, $\Delta_{fus}C_p$ as Determined From DSC Data; Molar Volume at T = 298.15 K, $V_m^{298.15}$

	T_{fus}	$\Delta_{fus}H$	T_{tr}	$\Delta_{tr}H$	$\Delta_{fus}C_p$	V_m(298.15 K)
compound	K	kJ·mol^{-1}	K	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	cm^3·mol^{-1}
1-decanol	279.14,[a] 279.3[b]	28.79[c]			101.20[d]	191.49
1-dodecanol	296.95,[c] 297.2[b]	38.42[c]			139.30[d]	224.70
cyclohexyl carboxylic acid	301.9,[e] 302.9[b]	9.197[e]				124.1[f]
cyclohexyl acetic acid	302.6,[e] 302.9[b]	13.802[e]				141.2[f]
cyclohexyl acetate	221.4,[e] 224.6[g]	3.384,[e] 7.994[g]	221.8,[g] 154 (g),[e] 151.8(g)[g]	5.230[g]	245.4[g]	146.6,[f] 147.3[h]
2-cyclohexyl ethyl acetate						179.2[f]
2-cyclohexyl ethanol						139.2[f]

[a] From ref 11. [b] From the SLE measurements. [c] From ref 12. [d] From interpolation of data for even-numbered 1-alkanols. [e] From ref 9. [f] Calculated from densities/Aldrich. [g] From ref 6. [h] From ref 7.

Solid−Liquid Phase Equilibria Apparatus and Measurements. Solid solubilities have been determined using a dynamic (synthetic) method described previously.[10] We prepared mixtures of solute and solvent 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 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 a calibrated Gallenkamp Autotherm II thermometer totally immersed in the thermostatting liquid. The measurements were carried out over a wide range of solute mole fraction from 0 to 1. We prepared mixtures 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 uncertainty of the temperature measurements was judged to be 0.1 K. The repeatability of the SLE experimental point was ± 0.1 K.

Results and Discussion

The brief characterization of 1-decanol or 1-dodecanol and FM is presented in Table 2. The experimental data of solid−liquid phase equilibria are listed in Tables 3 and 4 for 1-decanol and 1-dodecanol, respectively. Tables 3 and 4 include the direct experimental results of the SLE, temperatures, T_1/K versus x_1, the mole fraction of the solute, and γ_1, the activity coefficient of 1-alkanol in the saturated solution.

Experimental phase diagrams of SLE at ambient pressure investigated in this work are shown in Figures 1, 2, 3, 4, and 5. The solubility of CCA and CAA in 1-alkanols is dependent on the melting temperature, which is practically the same for both substances. At a high 1-alkanol mole fraction, the solubility of CAA is slightly higher in 1-decanol and lower in 1-dodecanol. These systems present simple eutectic systems with complete miscibility in the liquid phase. (See Figures 1 and 2.) The eutectic points were found graphically and are listed in Table 5. The eutectic temperatures of the systems {1-alkanol (1) + CCA or CAA (2)} increase with an increase in the 1-alkanol molecular weight and are shifted toward lower 1-alkanol mole fraction. (See Figure 5 for three 1-alkanols, including 1-octanol, measured previously.[9])

Similar results were observed in our earlier work for binary systems of 2,3-pentanedione (additive of butter) with 1-alkanols (1-hexadecanol, or 1-octadecanol, or 1-eicosanol).[13]

The eutectic points of the systems {1-alkanol (1) + CA or 2CEA or 2CE (2)} were shifted toward much lower 1-alkanol mole fraction in comparison with that of {1-alkanol (1) + CCA

Table 3. Experimental Solid−Liquid Phase Equilibrium Temperatures, *T*, for {1-Decanol (1) + FM (2)} Systems and Experimental Activity Coefficient of Solute, γ_1

x_1	T_1/K	γ_1	x_1	T_1/K	γ_1	x_1	T_1/K	γ_1
Cyclohexyl Carboxylic Acid								
0.0000	302.9	1.00	0.3945	277.5	1.18	0.5901	271.6	1.16
0.0418	300.3	1.01	0.3956	276.4	1.16	0.6382	273.0	1.15
0.1063	296.0	1.03	0.4518	273.3	1.22	0.6853	274.1	1.13
0.2058	289.6	1.06	0.4983	271.0	1.29	0.7961	276.5	1.09
0.2559	286.9	1.09	0.5152	269.3	1.18	0.9332	278.8	1.04
0.3499	280.4	1.14	0.5715	271.1	1.16	1.0000	279.3	1.00
Cyclohexyl Acetic Acid								
0.0000	302.9	1.00	0.4353	279.1	1.11	0.6675	272.5	1.07
0.0355	300.2	0.99	0.4735	275.6	1.12	0.6847	273.3	1.08
0.0845	297.8	0.99	0.4818	276.1	1.14	0.7418	274.4	1.06
0.1487	295.0	1.02	0.5253	273.0	1.16	0.7924	275.7	1.06
0.2107	292.7	1.05	0.5677	271.6	1.24	0.8714	277.7	1.06
0.2590	289.2	1.04	0.5691	271.3	1.24	0.9713	279.0	1.01
0.3260	285.7	1.07	0.6213	271.2	1.07	1.0000	279.3	1.00
0.3785	283.0	1.10	0.6446	272.1	1.08			
Cyclohexyl Acetate								
0.0804	255.7	3.70	0.3810	269.1	1.58	0.6638	274.3	1.17
0.0958	257.3	3.38	0.4086	269.7	1.52	0.7119	275.5	1.16
0.1157	258.9	3.05	0.4236	269.9	1.48	0.7540	276.2	1.14
0.1344	260.5	2.87	0.4657	270.7	1.40	0.7864	276.8	1.12
0.1551	261.9	2.67	0.4959	271.2	1.35	0.8642	277.7	1.07
0.1763	263.0	2.49	0.5007	271.3	1.34	0.8821	278.0	1.06
0.2006	264.1	2.32	0.5401	271.8	1.27	0.9204	278.2	1.03
0.2228	265.0	2.19	0.5510	272.4	1.29	0.9434	278.6	1.02
0.2720	266.8	1.96	0.5836	272.8	1.24	0.9568	278.8	1.02
0.3384	268.3	1.71	0.6235	273.4	1.20	1.0000	279.3	1.00
2-Cyclohexyl Ethyl Acetate								
0.0830	256.9	3.84	0.3064	268.0	1.86	0.6262	273.3	1.19
0.1056	259.3	3.42	0.3401	268.6	1.72	0.6777	274.4	1.16
0.1281	260.9	3.07	0.3691	269.1	1.63	0.7487	275.6	1.11
0.1511	263.0	2.90	0.4111	269.9	1.53	0.8120	276.7	1.08
0.1759	263.6	2.57	0.4476	270.8	1.46	0.8891	278.3	1.07
0.2025	265.0	2.41	0.4865	271.1	1.37	0.9481	278.9	1.03
0.2352	265.8	2.16	0.5285	271.8	1.30	1.0000	279.3	1.00
0.2685	266.6	1.97	0.5744	272.5	1.24			
2-Cyclohexyl Ethanol								
0.2188	253.8	1.22	0.4708	265.5	1.09	0.7429	272.8	1.07
0.2873	258.1	1.18	0.5187	267.3	1.08	0.8127	274.5	1.04
0.3217	260.6	1.20	0.5640	268.7	1.08	0.8805	276.2	1.00
0.3559	262.3	1.19	0.6150	269.9	1.00	0.9440	278.3	1.00
0.4237	264.1	1.10	0.6740	271.2	1.06	1.0000	279.3	1.00

Table 4. Experimental Solid−Liquid Phase Equilibrium Temperatures, *T*, for {1-Dodecanol (1) + FM (2)} Systems and Experimental Activity Coefficient of Solute, γ_1

x_1	T_1/K	γ_1	x_1	T_1/K	γ_1	x_1	T_1/K	γ_1
Cyclohexyl Carboxylic Acid								
0.0000	302.9	1.00	0.2949	283.8	1.11	0.6308	289.2	
0.0393	300.5	1.01	0.3148	282.9	1.12	0.7016	290.8	
0.0646	298.3	1.01	0.3568	281.0	1.16	0.7929	292.7	
0.1080	296.4	1.03	0.4013	282.3	1.11	0.8444	294.1	
0.1266	293.5	1.02	0.4134	282.7	1.11	0.9103	295.7	
0.1981	290.4	1.06	0.4800	284.5	1.05	1.0000	297.2	
0.2267	288.4	1.07	0.5543	286.6	1.02			
0.2753	285.9	1.11	0.5647	286.9	1.02			
Cyclohexyl Acetic Acid								
0.0000	302.9	1.00	0.3605	284.4	1.10	0.6295	289.2	
0.0734	299.1	1.00	0.3855	283.5	1.12	0.6716	290.5	
0.1177	296.9	1.02	0.4251	282.9	1.09	0.7558	293.0	
0.1717	294.2	1.03	0.4295	282.8	1.07	0.8471	294.8	
0.2295	291.3	1.05	0.4823	284.4	1.04	0.9235	296.4	
0.2863	289.4	1.09	0.4902	284.7	1.04	1.0000	297.2	
0.2941	288.3	1.08	0.5573	286.8	1.03			
0.3448	285.6	1.10	0.5811	287.7	1.04			
Cyclohexyl Acetate								
0.0542	267.2	3.32	0.3853	285.4	1.38	0.6359	290.3	1.09
0.0740	270.7	3.02	0.3993	285.7	1.36	0.6653	291.0	1.08
0.1009	273.7	2.67	0.4134	285.8	1.31	0.7002	291.3	1.05
0.1439	276.7	2.24	0.4301	286.3	1.30	0.7426	292.0	1.03
0.1777	278.0	1.96	0.4444	286.4	1.27	0.7779	292.8	1.02
0.2175	280.0	1.80	0.4637	286.8	1.24	0.7974	293.2	1.02
0.2408	281.3	1.75	0.4785	287.2	1.23	0.8344	293.7	1.00
0.2790	282.7	1.64	0.4960	287.6	1.21	0.8921	294.6	0.98
0.3029	283.4	1.57	0.5168	288.1	1.19	0.9264	295.5	0.99
0.3116	283.8	1.56	0.5333	288.5	1.18	0.9463	295.9	0.99
0.3303	284.1	1.49	0.5537	288.7	1.15	0.9793	296.6	0.99
0.3512	284.6	1.44	0.5800	289.2	1.13	1.0000	297.2	1.00
2-Cyclohexyl Ethyl Acetate								
0.0566	268.7	3.50	0.4246	285.7	1.27	0.7390	292.5	1.06
0.1033	274.7	2.78	0.4565	286.3	1.22	0.7530	292.7	1.05
0.1487	277.6	2.29	0.4885	287.2	1.20	0.7780	293.1	1.04
0.2106	280.7	1.94	0.5144	287.5	1.16	0.8104	293.9	1.04
0.2505	281.5	1.71	0.5510	288.3	1.13	0.8367	294.5	1.04
0.2637	282.0	1.66	0.5836	289.0	1.11	0.8590	294.7	1.02
0.2810	282.3	1.59	0.6150	289.7	1.09	0.9090	295.5	1.00
0.2955	283.3	1.60	0.6264	289.9	1.09	0.9351	295.7	0.99
0.3146	283.7	1.54	0.6542	290.4	1.07	0.9500	296.1	0.99
0.3313	284.0	1.48	0.6700	291.1	1.08	0.9510	296.2	1.00
0.3504	284.3	1.43	0.6914	291.4	1.06	1.0000	297.2	1.00
0.3701	284.8	1.39	0.7090	292.0	1.07			
2-Cyclohexyl Ethanol								
0.3174	279.0	1.16	0.5185	286.7	1.09	0.7439	293.2	1.07
0.3692	281.1	1.13	0.5710	288.2	1.08	0.8254	294.7	1.04
0.4199	283.2	1.12	0.6277	290.0	1.08	0.9041	296.1	1.00
0.4726	284.9	1.09	0.6848	291.4	1.00	1.0000	297.2	1.00

or CAA (2)} and were not measured. The polar carboxylic substituent in the CCA and CAA molecules is responsible for the strong interaction with 1-alkanol. Changing the substitution group on the cyclohexane ring from −COOH to $-CH_2COOH$ shifts the eutectic composition to a higher 1-alkanol mole fraction. (See Figures 1 and 2.) This is a result of a lower solubility of CAA in 1-alkanol and could be revealed from steric effects.

The solubilities of the other two compounds, CA and 2CEA (which are liquid at room temperature), in 1-alkanols are similar and depend mainly on the melting temperature of 1-alkanol. (See Figures 3 and 4.) The liquidus curves of CA and 2CEA are very close to each other, and only 2CE reveals better solubility. This can be an effect of the hydrogen bonding between the hydroxyl group of 2CE and 1-alkanol.

The solid−solid phase transition of CA (known from literature)[6] was not observed during the SLE measurements. (See Figures 3 and 4.)

Experimental phase diagrams of SLE with FM investigated in this work reveal the simple eutectic systems with complete miscibility in the liquid phase with a solubility lower than the ideal one. (See the values of activity coefficients described below in Tables 3 and 4 and liquidus curves in Figure 4.) The solubility decreases with an increase in the number of carbon atoms of 1-alkanol; the eutectic points shift to the lower mole fraction of 1-alkanol when the melting point of 1-alkanol increases.

Correlation of Solid−Liquid Equilibrium. The solubility of a solid 1 in a liquid may be expressed in a very general manner by eq 1

$$-\ln x_1\gamma_1 = \frac{\Delta_{\mathrm{fus}}H_1}{R}\left(\frac{1}{T_1} - \frac{1}{T_{\mathrm{fus},1}}\right) - \frac{\Delta_{\mathrm{fus}}C_{p_1}}{R}\left(\ln\frac{T_1}{T_{\mathrm{fus},1}} + \frac{T_{\mathrm{fus},1}}{T_1} - 1\right) \quad (1)$$

where x_1, γ_1, $\Delta_{\mathrm{fus}}H_1$, $\Delta_{\mathrm{fus}}C_{p_1}$, $T_{\mathrm{fus},1}$, and T_1 stand for mole fraction, activity coefficient, enthalpy of fusion, difference in solute (here 1-decanol and 1-dodecanol) heat capacity between the liquid

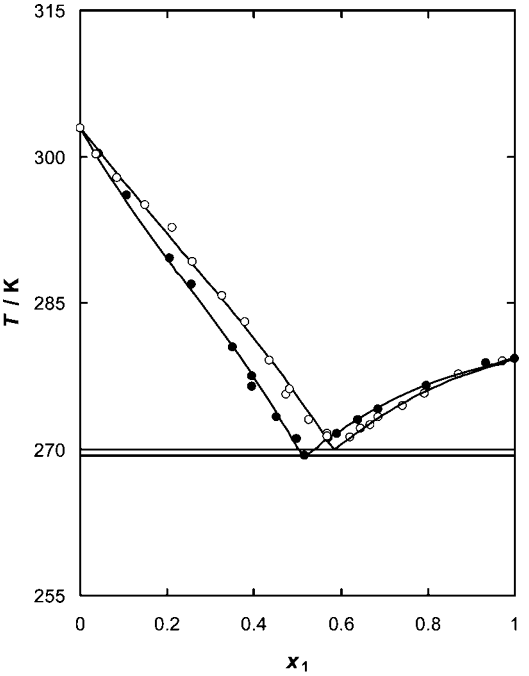


Figure 1. Solid−liquid phase equilibria of {1-decanol (1) + FM (2)} binary systems: ●, cyclohexyl carboxylic acid; ○, cyclohexyl acetic acid. Equilibrium temperature, *T*, against the 1-decanol mole fraction, x_1. Solid line designated by the Wilson equation.

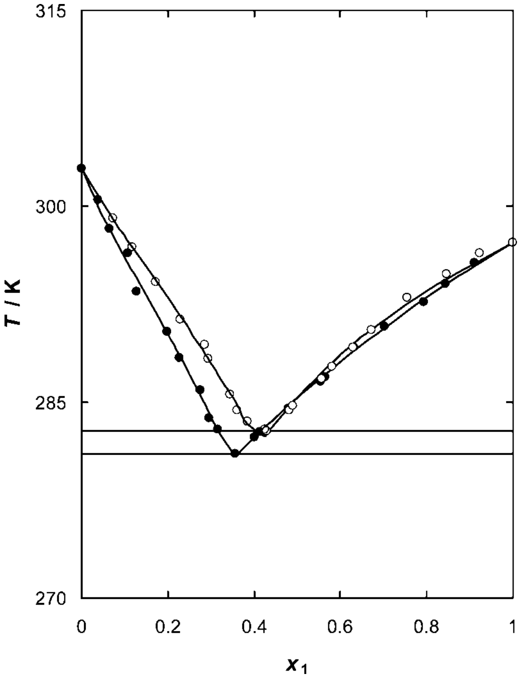


Figure 2. Solid−liquid phase equilibria of {1-dodecanol (1) + FM (2)} binary systems: ●, cyclohexyl carboxylic acid; ○, cyclohexyl acetic acid. Equilibrium temperature, *T*, against the 1-decanol mole fraction, x_1. Solid line designated by the Wilson equation.

and solid at the melting temperature, melting temperature of the solute (1), and equilibrium temperature, respectively. Equation 1 may be used assuming simple eutectic behavior with full miscibility in the liquid phase and immiscibility in the solid phase.

In this study, two methods were used to derive the solute activity coefficients, γ_1 from the correlation equations that describe the Gibbs energy of mixing (G^E): the Wilson[14] equation and the nonrandom two-liquid (NRTL) equation.[15]

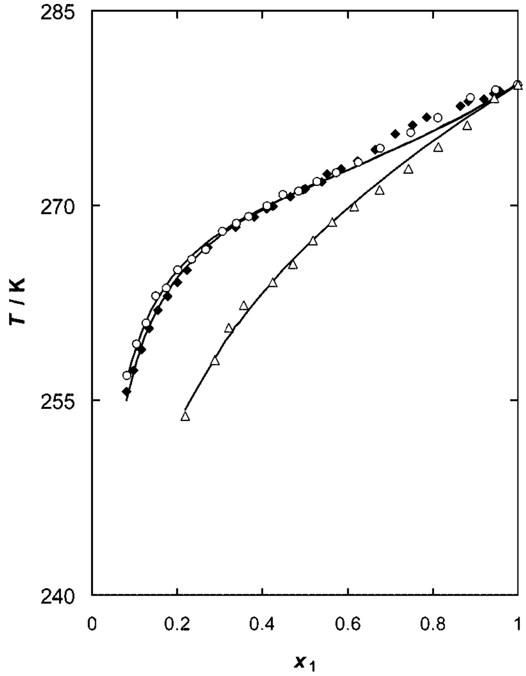


Figure 3. Solid−liquid phase equilibria of {1-decanol (1) + FM (2)} binary systems: ◆, cyclohexyl acetate; ○, 2-cyclohexyl ethyl acetate; △, 2-cyclohexyl ethanol. Equilibrium temperature, *T*, against the 1-decanol mole fraction, x_1. Solid line designated by the Wilson equation.

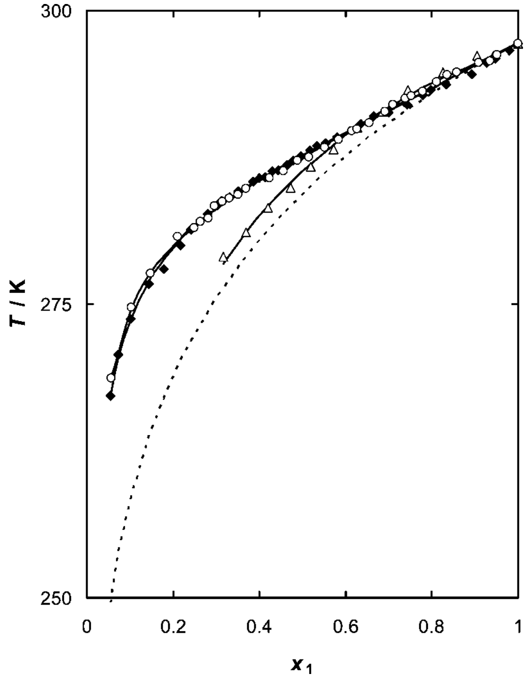


Figure 4. Solid−liquid phase equilibria of {1-dodecanol (1) + FM (2)} binary systems: ◆, cyclohexyl acetate; ●, 2-cyclohexyl ethyl acetate; △, 2-cyclohexyl ethanol. Equilibrium temperature, *T*, against the 1-dodecanol mole fraction, x_1. Solid line designated by the Wilson equation. Dotted line represents an ideal solubility.

Two adjustable parameters of the equations were found by an optimization technique. The objective function was as follows

$$F(A_1A_2) = \sum_{i=1}^{n} w_i^{-2}[\ln x_{1i}\gamma_{1i}(T_i, x_{1i}, A_1A_2) - \ln a_{1i}]^2 \quad (2)$$

where $\ln a_{1i}$ denotes an "experimental" value of the logarithm of the solute activity, taken as the left-hand side of eq 1, w_i is

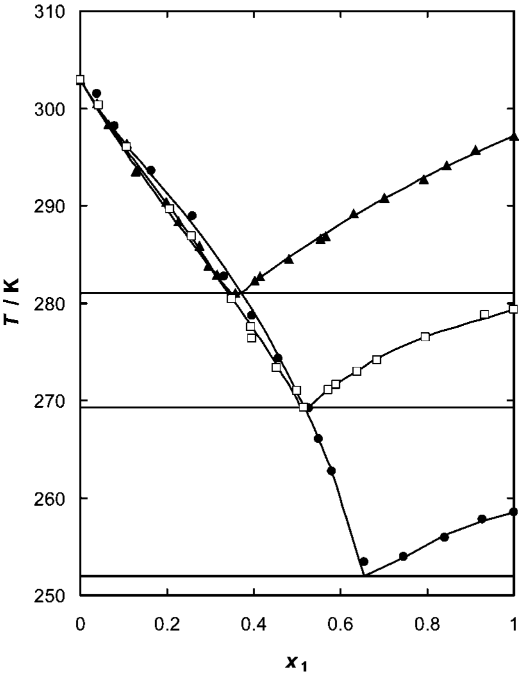


Figure 5. Solid−liquid phase equilibria of {1-alkanol (1) + cyclohexyl carboxylic acid (2)} binary systems: ●, 1-octanol;[9] □, 1-decanol; ▲, 1-dodecanol. Solid line designated by the Wilson equation.

Table 5. Eutectic Temperatures, $T_{1,e}$, and Compositions, $x_{1,e}$, Detected Graphically for {1-Decanol or 1-Dodecanol (1) + CCA or CAA (2)} Binary Systems

FM	$x_{1,e}$	$T_{1,e}$/K
1-Decanol		
cyclohexyl carboxylic acid	0.520	269.1
cyclohexyl acetic acid	0.592	269.7
1-Dodecanol		
cyclohexyl carboxylic acid	0.365	280.6
cyclohexyl acetic acid	0.410	281.9

the weight of an experimental point, A_1 and A_2 are the two adjustable parameters of the correlation equations, i denotes the ith experimental point, and n is the number of experimental data. The weights were calculated by means of the error propagation formula

$$w_i^2 = (\partial \ln x_1\gamma_1 - \partial \ln a_i)/(\partial T)^2_{T=T_i}(\Delta T_i)^2 + ((\partial \ln x_1\gamma_1)/(\partial x_1))^2_{x_1=x_{1i}}(\Delta x_{1i})^2 \quad (3)$$

where ΔT and Δx_1 are the estimated errors in T and x_{1i}, respectively. A_1 and A_2 are model parameters resulting from the minimization procedure. The root-mean-square deviation of temperature was defined as follows

$$\sigma_T = \left(\sum_{i=1}^{n} \frac{\left(T_i^{\text{exptl}} - T_i^{\text{calcd}}\right)^2}{n-2}\right)^{\frac{1}{2}} \quad (4)$$

The correlation was presented with the development of two adjustable parameters. In this work, the value of 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 6.)

Table 6. Correlation of the Solid−Liquid Phase Equilibrium Data of the {1-Decanol or 1-Dodecanol (1) + Fragrance Material (2)} Binary Mixtures by Means of the Wilson and NRTL Equations: Values of Parameters and Measures of Deviation

	Wilson	NRTL
compound (2)	g_{12-22} g_{21-11} J·mol^{-1} $(\sigma_T/\text{K})^a$	g_{12-22} g_{21-11} J·mol^{-1} $(\sigma_T/\text{K})^a$
1-Decanol		
cyclohexyl carboxylic acid	−2750.98	3876.11^b
	7280.76	−646.00
	(0.19)	(0.22)
cyclohexyl acetic acid	−2885.69	3770.88^b
	6788.36	−1183.58
	(0.19)	(0.21)
cyclohexyl acetate	1887.48	1921.39^c
	1908.96	2634.50
	(0.55)	(0.43)
2-cyclohexyl ethyl acetate	2691.95	2005.87^c
	1367.03	2967.46
	(0.44)	(0.34)
2-cyclohexyl ethanol	978.59	−1162.06^d
	153.69	2473.84
	(0.52)	(0.51)
1-Dodecanol		
cyclohexyl carboxylic acid	15702.4	−228.03^c
	68.99	4782.76
	(0.19)	(0.19)
cyclohexyl acetic acid	−2907.03	2232.71^b
	4799.01	−959.01
	(0.38)	(0.39)
cyclohexyl acetate	2100.04	757.61^c
	1206.84	2716.0
	(0.24)	(0.24)
2-cyclohexyl ethyl acetate	3082.81	711.84^c
	584.72	3081.23
	(0.22)	(0.22)
2-cyclohexyl ethanol	−2754.46	2516.57^b
	5158.86	−739.65
	(0.38)	(0.39)

[a] According to eq 4. [b] α = 0.9. [c] α = 0.7. [d] α = 0.3.

Values of model parameters obtained by fitting solubility curves together with the corresponding standard deviations are given in Table 6. For systems under study, the description of the solid−liquid phase equilibrium was given by the average standard mean deviation (σ_T) equal to (0.33 and 0.31) K for Wilson and NRTL equations, respectively. The comparison of the experimental points with the Wilson equation is shown in Figures 1, 2, 3, 4, and 5.

Positive deviations from ideality were found. The values of activity coefficients in the saturated solution of 1-alkanol in CCA and CAA were very close to one, $\gamma_1 \approx 1$. (See Tables 3 and 4.) The higher the deviations from the ideality, the higher the values of activity coefficients. The values $\gamma_1 > 1$ were observed for CA, 2CEA, and 2CE at very low concentration of 1-alkanol. It is generally known that for small solubility, the activity coefficients are higher than one.

Conclusions

New thermodynamic data on solid−liquid phase equilibria of 1-decanol and 1-dodecanol with five polar fragrance raw materials based on cyclohexane were presented. These phase diagrams have shown simple eutectic mixtures. In general, the binary mixtures investigated in this work reveal complete miscibility in the liquid phase, which is a result of the molecular interaction of the polar substituents of the fragrance materials and polar solvent long chain alcohols. The solubility decreases as the alkyl chain of the 1-alkanol increases. The results of the correlation were obtained with very low standard deviation and were similar for two equations used.

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