Quaternary System Nitromethane + 1-Hexanol + Octanoic Acid + 1,2,3-Propanetriol with Three Liquid Phases

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The mutual solubilities for nitromethane + 1-hexanol + octanoic acid + 1,2,3-propanetriol have been studied in the temperature range 10.3 °C to 118.6 °C by the synthetic method. Phase diagrams are reported over this temperature range. A discussion of the variation of the phase behavior of the two three-liquid-phase regions with temperature is given.

Relatively few data exist for systems comprised of four liquid components. Data for some quaternary systems with three liquid phases have been published.[1] In a quaternary mixture, the composition may be expressed as a set of three independent mole fractions, and the isothermal phase diagram, in these variables, is conveniently represented in a composition tetrahedron. If a given mixture shows separation into three phases, there is a corresponding triangle inside the tetrahedron whose vertices represent the three sets of mole fractions, which specify the compositions of the coexistent phases. A stack of such triangles delineates the whole three-phase region at the given temperature. These three-phase regions may be disposed between the face of the tetrahedron and the critical-end-point tie line (for example, benzene + heptane + aniline + water system[2]) or may be completely in the interior of the tetrahedron and disposed between the two critical-end-point tie lines, as in the water + acetonitrile + benzene + hexane system.[3]

In the present paper we present results of the mutual solubility of the quaternary system nitromethane (A) + 1-hexanol (B) + octanoic acid (C) + 1,2,3-propanetriol (D), and two ternary systems with equilibrium between three liquid phases—nitromethane + 1-hexanol + 1,2,3-propanetriol and nitromethane + octanoic acid + 1,2,3-propanetriol—between 10.3 °C and 118.6 °C are reported. No data about this quaternary system was found in the literature. However, solubility data for both ternary systems were previously published.[4−5]

Experimental Section

Nitromethane (pure grade; Reakhim, Russia) was dried over molecular sieves Type 4A and distilled twice through a column of 20 theoretical plates packed with glass spirals 5 mm in diameter.

1-Hexanol (pure grade; Reakhim, Russia) was dried over CaO and distilled repeatedly through a column of 60 theoretical plates packed with steel rings 3 mm in diameter. Octanoic acid (pure grade; Reakhim, Russia) was dried over molecular sieves Type 4A and repeatedly fractionally distilled at about 270 Pa. 1,2,3-Propanetriol (for microscopy, Merck) was repeatedly fractionally distilled at about 100 Pa. The purity of the materials was determined by GLC. Table 1 shows the densities and refractive indices of the pure components together with those reported in the literature for comparison.

Table 1. Experimental Values of Density (ρ) and Refractive Index (n_D) of Pure Components at 20.0 °C

compd	ρ/kg·m^{-3} exptl	ρ/kg·m^{-3} lit.	n(D) exptl	n(D) lit.
nitromethane	1138.1	1137.9[6]	1.3819	1.381 89[6]
1-hexanol	819.7	818.6[6]	1.4182	1.418 16[7]
octanoic acid	909.0	908.94[6]	1.4279	1.427 9[6]
1,2,3-propanetriol	1261.3	1261.34[6]	1.4740	1.473 99[6]

Heterogeneous ternary and quaternary mixtures were prepared gravimetrically in glass ampules with an internal diameter of 20 mm and height of 70 mm. Mole fractions were estimated to have been accurate to ±0.0005. The three liquid phases involved in these mixtures are labeled as the propanetriol-rich, nitromethane-rich, and alcohol-rich or acid-rich phases, corresponding to the lower, middle, and upper phases from the point of view of density. The ternary and quaternary mixtures had a constant mole content of D of 0.1 or 0.4. In the quaternary mixtures there was a constant mole relationship of B and C (x_B/x_C = constant) of 1:6.4, 1:2.8, 1:1.1, 3.3:1, or 8:1. The total mass of the mixture was (8 to 11) g, depending on the overall composition. The solubility curves of the ternary and quaternary systems were determined by a synthetic (cloud-point) method. The temperatures of transition from the three-phase region to the two-phase region and from the two-phase region to the one-phase region are found for mixtures of various compositions. From these measurements the composition of the mixture reaching the three-phase state at the highest temperature may be determined. The sealed ampules (in pairs in the special holder) were put into a 30-L water thermostat with transparent sides and were heated with vigorous stirring of water, and the shaking ampules were heated to a temperature somewhat higher than the solubility temperature of the three liquid phases and then slowly cooled at a rate of about 0.1 K min^{-1} until turbidity appeared. Heating and cooling cycles were repeated twice. Values of the temperature of phase transition obtained for appearing and disappearing turbidity were averaged. These points were recorded as the cloud-point temperature and plotted against the mole fraction of nitromethane. The temperature variations in the temperature range 10.3 °C to 31.5 °C were ±0.05 °C (Table 2), according to a set of calibrated mercury thermometers TR-2 (Russia) with 0.01 °C scale divisions. The thermometers

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Table 2. Temperatures of the Three Liquid Phases in the Quaternary System Nitromethane (A) + 1-Hexanol (B) + Octanoic Acid (C) + 1,2,3-Propanetriol (D) and Two Ternary Systems A + B + D and A + C + D[a]

intersection x_D = 0.1				
t/°C	x_A	x_B	x_C	x_D
Ternary System Nitromethane (A) + Octanoic Acid (C) + 1,2,3-Propanetriol (D)				
14.6	0.453		0.447	0.100
19.1	0.504		0.396	0.100
21.6	0.551		0.349	0.100
23.4	0.593		0.307	0.100
24.5	0.633		0.267	0.100
25.1	0.670		0.230	0.100
25.3	0.705*		0.195*	0.100*
25.3	0.720		0.180	0.100
25.3	0.734		0.166	0.100
25.2	0.763		0.137	0.100
24.6	0.791		0.109	0.100
23.1	0.818		0.092	0.100
19.2	0.841		0.059	0.100
12.7	0.862		0.038	0.100
		x_B/x_C = 1:6.4		
12.8	0.447	0.062	0.391	0.100
16.5	0.497	0.054	0.349	0.100
19.1	0.542	0.049	0.309	0.100
20.8	0.578	0.043	0.279	0.100
22.1	0.622	0.038	0.240	0.100
22.8	0.658	0.033	0.209	0.100
23.1	0.693	0.028	0.179	0.100
23.3	0.709*	0.026*	0.165*	0.100*
23.2	0.724	0.024	0.152	0.100
22.9	0.754	0.020	0.126	0.100
22.1	0.782	0.016	0.102	0.100
20.6	0.810	0.012	0.078	0.100
17.9	0.833	0.009	0.058	0.100
11.3	0.856	0.006	0.038	0.100
		x_B/x_C = 1:2.8		
11.8	0.439	0.120	0.341	0.100
15.4	0.487	0.108	0.305	0.100
17.6	0.533	0.096	0.271	0.100
19.5	0.575	0.085	0.240	0.100
20.8	0.615	0.074	0.211	0.100
21.4	0.651	0.065	0.184	0.100
21.8	0.686	0.056	0.158	0.100
21.9	0.702*	0.052*	0.146*	0.100*
21.9	0.718	0.048	0.134	0.100
21.5	0.748	0.040	0.112	0.100
20.6	0.778	0.032	0.090	0.100
19.0	0.806	0.025	0.070	0.100
16.1	0.831	0.018	0.051	0.100
10.3	0.854	0.012	0.034	0.100
		x_B/x_C = 1:1.1		
11.6	0.420	0.233	0.247	0.100
15.0	0.469	0.209	0.222	0.100
17.4	0.516	0.186	0.198	0.100
19.1	0.558	0.166	0.176	0.100
20.3	0.600	0.146	0.155	0.099
21.2	0.638	0.127	0.135	0.100
21.6	0.673	0.110	0.117	0.100
21.7	0.692*	0.101*	0.107*	0.100*
21.7	0.708	0.093	0.099	0.100
21.3	0.739	0.078	0.083	0.100
20.5	0.770	0.063	0.067	0.100
19.2	0.799	0.049	0.052	0.100
16.4	0.826	0.036	0.038	0.100
12.0	0.852	0.023	0.025	0.100
		x_B/x_C = 3.3:1		
15.3	0.340	0.427	0.133	0.100
18.8	0.394	0.388	0.118	0.100
21.5	0.445	0.349	0.106	0.100
23.4	0.493	0.312	0.095	0.100
24.9	0.536	0.279	0.085	0.100
25.8	0.578	0.247	0.075	0.100
26.4	0.618	0.216	0.066	0.100
26.6	0.656*	0.187*	0.057*	0.100*
26.6	0.674	0.173	0.053	0.100
26.5	0.691	0.160	0.049	0.100
26.1	0.725	0.134	0.041	0.100
25.0	0.759	0.108	0.033	0.100
23.4	0.789	0.085	0.026	0.100
20.5	0.819	0.062	0.019	0.100
14.4	0.846	0.041	0.013	0.100

intersection x_D = 0.4				
t/°C	x_A	x_B	x_C	x_D
Ternary System Nitromethane (A) + Octanoic Acid (C) + 1,2,3-Propanetriol (D)				
10.4	0.266		0.335	0.400
14.8	0.303		0.297	0.400
17.9	0.336		0.264	0.400
20.9	0.367		0.233	0.400
23.0	0.395		0.205	0.400
24.3	0.422		0.178	0.400
25.0	0.445		0.155	0.400
25.2	0.470		0.130	0.400
25.3	0.480*		0.120*	0.400*
25.3	0.489		0.111	0.400
25.2	0.498		0.102	0.400
25.1	0.510		0.090	0.400
24.7	0.528		0.072	0.400
23.1	0.543		0.057	0.400
19.4	0.557		0.043	0.400
11.7	0.574		0.026	0.400
		x_B/x_C = 1:6.4		
13.3	0.306	0.040	0.254	0.400
16.6	0.335	0.036	0.229	0.400
19.5	0.362	0.032	0.207	0.399
21.3	0.387	0.029	0.185	0.400
22.6	0.411	0.025	0.164	0.400
23.1	0.434	0.022	0.144	0.400
23.2	0.456	0.019	0.125	0.400
23.2	0.466*	0.018*	0.116*	0.400*
23.1	0.476	0.017	0.107	0.400
23.0	0.486	0.015	0.099	0.400
22.9	0.497	0.014	0.089	0.400
22.4	0.513	0.012	0.075	0.400
21.1	0.524	0.009	0.057	0.400
17.1	0.549	0.007	0.044	0.400
10.6	0.570	0.004	0.026	0.400
		x_B/x_C = 1:2.8		
12.6	0.298	0.079	0.223	0.400
15.4	0.327	0.071	0.202	0.400
17.8	0.354	0.064	0.182	0.400
19.8	0.379	0.058	0.163	0.400
21.1	0.405	0.051	0.144	0.400
21.8	0.428	0.045	0.127	0.400
22.0	0.450	0.039	0.110	0.401
22.0	0.461*	0.036*	0.103*	0.400*
21.9	0.473	0.033	0.094	0.400
21.8	0.482	0.031	0.087	0.400
21.6	0.492	0.028	0.080	0.400
20.8	0.512	0.023	0.065	0.400
18.9	0.531	0.018	0.051	0.400
15.5	0.550	0.013	0.037	0.400
		x_B/x_C = 1:1.1		
12.3	0.282	0.154	0.164	0.400
15.1	0.313	0.140	0.148	0.399
17.4	0.342	0.126	0.133	0.399
19.5	0.367	0.113	0.120	0.400
21.0	0.393	0.100	0.107	0.400
21.7	0.417	0.089	0.094	0.400
21.8	0.441	0.077	0.082	0.400
21.8	0.452*	0.072*	0.076*	0.400*
21.7	0.463	0.066	0.070	0.400
21.6	0.476	0.060	0.064	0.400
21.4	0.487	0.055	0.058	0.400
20.5	0.505	0.046	0.049	0.400
18.4	0.526	0.036	0.038	0.400
15.0	0.546	0.026	0.028	0.400
		x_B/x_C = 3.3:1		
13.4	0.227	0.285	0.087	0.401
17.4	0.260	0.261	0.079	0.400
20.4	0.291	0.237	0.072	0.400
22.9	0.320	0.215	0.065	0.400
24.8	0.348	0.193	0.059	0.400
25.8	0.375	0.173	0.052	0.400
26.3	0.402	0.152	0.046	0.400
26.5	0.427	0.132	0.040	0.401
26.6	0.438	0.124	0.038	0.400
26.6	0.450*	0.116*	0.035*	0.399*
26.5	0.463	0.105	0.032	0.400
26.4	0.476	0.096	0.029	0.399
25.8	0.497	0.079	0.024	0.400
24.7	0.519	0.062	0.019	0.400
21.3	0.540	0.046	0.014	0.400
14.0	0.561	0.030	0.009	0.400

Table 2 (Continued)

intersection $x_D = 0.1$					intersection $x_D = 0.4$				
t/°C	x_A	x_B	x_C	x_D	t/°C	x_A	x_B	x_C	x_D
		$x_B/x_C = 8:1$					$x_B/x_C = 8:1$		
14.4	0.274	0.556	0.070	0.100	18.1	0.217	0.340	0.043	0.400
19.3	0.331	0.506	0.063	0.100	22.0	0.250	0.311	0.039	0.400
22.9	0.383	0.459	0.058	0.100	24.6	0.281	0.283	0.036	0.400
25.0	0.433	0.415	0.052	0.100	26.8	0.311	0.257	0.032	0.400
26.7	0.480	0.373	0.047	0.100	27.8	0.340	0.232	0.029	0.399
27.8	0.525	0.334	0.041	0.100	28.4	0.367	0.207	0.026	0.400
28.4	0.568	0.295	0.037	0.100	28.7	0.394	0.183	0.023	0.400
28.7	0.609	0.259	0.032	0.100	28.8	0.420	0.160	0.020	0.400
28.7	0.647*	0.225*	0.028*	0.100*	28.8	0.436*	0.146*	0.018*	0.400*
28.6	0.665	0.209	0.026	0.100	28.7	0.445	0.138	0.017	0.400
28.4	0.684	0.192	0.024	0.100	28.5	0.457	0.127	0.016	0.400
27.7	0.719	0.161	0.020	0.100	28.2	0.469	0.116	0.015	0.400
26.5	0.755	0.129	0.016	0.100	27.6	0.493	0.095	0.012	0.400
24.7	0.784	0.103	0.013	0.100	25.7	0.518	0.073	0.009	0.400
21.8	0.818	0.073	0.009	0.100	22.3	0.538	0.055	0.007	0.400
16.1	0.845	0.049	0.006	0.100	15.1	0.563	0.033	0.004	0.400
	Ternary System Nitromethane (A) + 1-Hexanol (B) + 1,2,3-Propanetriol (D)					Ternary System Nitromethane (A) + 1-Hexanol (B) + 1,2,3-Propanetriol (D)			
11.2	0.205	0.695		0.100	14.9	0.178	0.422		0.400
16.7	0.266	0.634		0.100	21.0	0.215	0.385		0.400
21.5	0.323	0.577		0.100	25.5	0.250	0.350		0.400
25.0	0.376	0.524		0.100	28.5	0.285	0.315		0.400
27.4	0.427	0.473		0.100	29.6	0.305	0.295		0.400
29.2	0.475	0.425		0.100	30.5	0.332	0.268		0.400
30.6	0.520	0.380		0.100	31.1	0.363	0.237		0.400
31.3	0.563	0.337		0.100	31.4	0.403	0.197		0.400
31.5	0.604*	0.296*		0.100*	31.5	0.428*	0.172*		0.400*
31.4	0.645	0.255		0.100	31.4	0.442	0.158		0.400
31.4	0.663	0.237		0.100	31.3	0.460	0.140		0.400
31.3	0.681	0.219		0.100	31.1	0.472	0.128		0.400
30.8	0.717	0.183		0.100	30.8	0.484	0.116		0.400
29.5	0.753	0.147		0.100	29.9	0.499	0.101		0.400
27.2	0.786	0.114		0.100	27.8	0.523	0.077		0.400
23.9	0.817	0.083		0.100	24.1	0.545	0.055		0.400
17.4	0.846	0.054		0.100	16.8	0.567	0.033		0.400

[a] Values marked with asterisks correspond to the composition of ternary or quaternary mixtures in which two liquid phases become critical in the presence of a third liquid phase. x_i is the mole fraction of component i in the mixture.

were checked against a standard temperature and agreed with each other within the set. These checks were made on a factory "Thermometer". By a similar way at the further increase of temperature, we have defined the solubility temperatures of the two liquid phases for the ternary and quaternary mixtures with $x_D = 0.1$.

Results and Discussion

The experimental values of the solubility temperatures of the three liquid phases for two ternary and quaternary systems are given in Table 2. The three-component nitromethane + 1-hexanol + 1,2,3-propanetriol and nitromethane + octanoic acid + 1,2,3-propanetriol mixtures have a three-phase region at room temperature. The upper meniscus is associated with the binary nitromethane + 1-hexanol (octanoic acid) solutions with critical temperatures 35.6 °C and 35.0 °C, respectively,[8] and the lower meniscus with the nitromethane + 1,2,3-propanetriol solution with a separation temperature of about 133 °C.[5] The maximal temperature of the three-phase liquid equilibrium in these ternary subsystems was determined as 31.5 °C and 25.3 °C, respectively. At these temperatures two liquid phases (nitromethane-rich and alcohol-rich or acid-rich) become critical in the presence of a third phase (propanetriol-rich) and the triangle with vertices corresponding to the concentrations of the three liquid phases reduces to a straight line which is called the critical-end-point tie line.[3] Figure 1 shows an example of the temperature at which the second meniscus disappears as a function of nitromethane concentration for two ternary mixtures A + B + D and A + C + D and some quaternary mixtures with $x_D = 0.1$ and $x_D = 0.4$. Curves of this type are called the polytherms of solubility.[9] On this basis the three-phase regions may be determined for a given intersection of the composition tetrahedron for any arbitrary temperature. The curves approximating the solubility temperatures of the two liquid phases for ternary and some quaternary mixtures (at $x_D = 0.1$) with the mole fraction of nitromethane are shown in Figure 2. For each curve the ratio of the mole fractions of alcohol and acid, as well the mole content of 1,2,3-propanetriol, is fixed. The borders of the

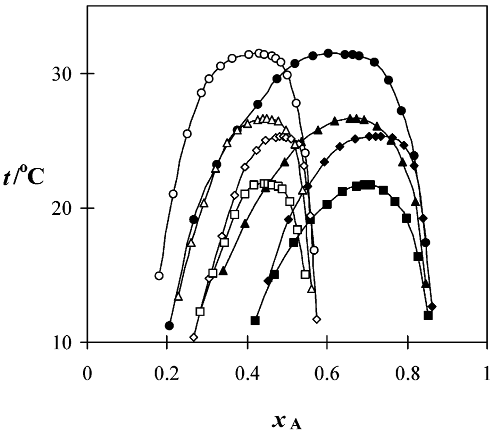

Figure 1. Solubility temperatures of the three liquid phases as a function of nitromethane concentration for two ternary and quaternary solutions of 1,2,3-propanetriol concentration $x_D = 0.1$ (black markers) and 0.4 (white markers). Ternary nitromethane + 1-hexanol + 1,2,3-propanetriol (○) and nitromethane + octanoic acid + 1,2,3-propanetriol (◇) mixtures. Constant mole fraction ratios of 1-hexanol to octanoic acid (x_B/x_C) in quaternary mixtures: □, 0.91; △, 3.3.

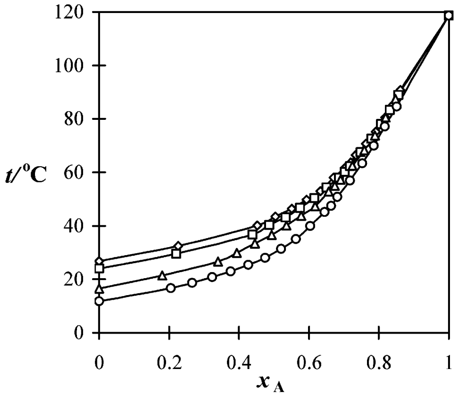

Figure 2. Experimental solubility of the two liquid phase curves for the nitromethane + 1-hexanol + 1,2,3-propanetriol (○) and nitromethane + octanoic acid + 1,2,3-propanetriol (◇) ternary and quaternary systems with $x_D = 0.1$. Constant mole fraction ratios of 1-hexanol to octanoic acid (x_B/x_C) in quaternary mixtures: □, 0.36; △, 3.3.

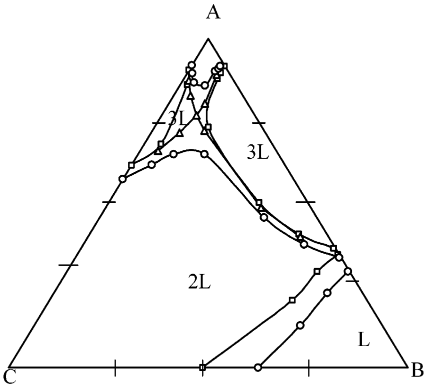

Figure 3. Isothermal projections of two-phase and three-phase regions on the nitromethane + 1-hexanol + octanoic acid face for an intersection of the tetrahedron corresponding to 0.1 mole fraction 1,2,3-propanetriol. Temperature (°C): ○, 20.0; △, 21,4; and □, 22.0.

two-phase and three-phase regions were determined at (20.0, 21.4, and 22.0) °C using the graphical interpolation from Figures 1 and 2. The results of interpolation are presented in Figure 3.

As the binary boundary subsystems A + B, A + C, A + D, B + D, and C + D have limited miscibility, with upper critical solution temperatures, on cooling, the mutual solubility in the ternary and quaternary systems decreases. In the temperature range 31.5 °C to 25.3 °C in the composition tetrahedron of the quaternary system, there exists only one region where there is equilibrium between three liquid phases. This region lies between the face A + B + D of the tetrahedron and the critical-end-point tie line. Below 25.3 °C the second region of three-phase equilibrium appears which abuts the face A + C + D of the tetrahedron and the other critical-end-point tie line. As is obvious (visible) from Figure 3, two regions of three-phase equilibrium continuously come nearer to each other, and then at a certain temperature they come into contact by their critical-end-point tie line. This temperature is determined as (21.4 ± 0.1) °C from the curves connecting all points to the composition of the ternary or quaternary mixtures at which two liquid phases become critical in the presence of a third liquid phase, which is presented in Figure 4. The lowest temperature on these curves for the intersections of the tetrahedron at $x_D = 0.1$ and 0.4 is 21.4 °C. At the subsequent coalescence of two regions of the three-phase equilibrium, one region of equilibrium of three liquid phases is formed. At a temperature near 21.4 °C (a little bit higher or a little bit below), the isothermal projections of the three-phase regions on the face nitromethane + 1-hexanol + octanoic acid of the tetrahedron represent two pairs of curves with opposite sign, similar to the isothermal solubility curves of the ternary system A + B + C in the temperature region near 29.7 °C.[8]

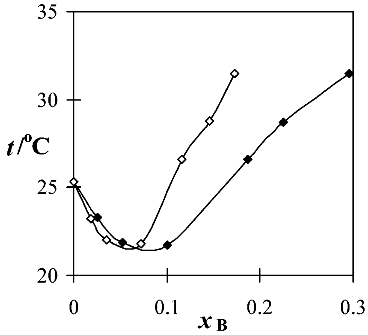

Figure 4. Curves connecting all points to the composition of ternary or quaternary mixtures (Table 2) at which two liquid phases become critical in the presence of a third liquid phase. Content of 1,2,3-propanetriol in these mixtures: ◆, 0.1; ◇, 0.4 mole fraction.

At 31.5 °C and higher in the quaternary system nitromethane + 1-hexanol + octanoic acid + 1,2,3-propanetriol and in all ternary subsystems, there is no equilibrium of three liquid phases. Above 35.6 °C, the ternary subsystem A + B + C is homogeneous, and three other ternary subsystems have a region of band-type immiscibility. In the tetrahedron of the quaternary system there is a region of two-phase equilibrium, which is disposed between three faces of the tetrahedron.

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