

because these selectivities are much greater than 1 (between 1.3 and 17.4). This conclusion is also reflected in Figure 5, where the selectivity curves are located well above the bisectrix, which represented the unity. Compared with solvents such as 1-pentanol, 1-propanol, and methyl-1-butanol, tributyl phosphate can be considered as a solvent more suitable for extraction of malic acid from wastewater.

Glossary

w_{AR}	mass fraction of water in the aqueous phase
w_{BR}	mass fraction of malic acid in the aqueous phase
w_{SR}	mass fraction of solvent in the aqueous phase
w_{AE}	mass fraction of water in the organic phase
w_{BE}	mass fraction of malic acid in the organic phase
w_{SE}	mass fraction of solvent in the organic phase
m	partition coefficient = w_{BE}/w_{BR}
β	selectivity = $(w_{BE}/(w_{BE} + w_{AE})) / (w_{BR}/(w_{BR} + w_{AR}))$

S solid phase
L liquid phase

Registry No. Malic acid, 6915-15-7; tributyl phosphate, 126-73-8.

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Liquid-Liquid Equilibria for the Systems Perfluorodecalin + Heptane + 1-Hexene, Perfluorodecalin + 1-Hexene + Hexane, and Perfluorodecalin + Heptane + 1-Hexene + Hexane

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Liquid-liquid equilibria for the quaternary system perfluorodecalin + heptane + 1-hexene + hexane at 288.15 and 298.15 K and for the ternary systems perfluorodecalin + heptane + 1-hexene at 288.15, 298.15, and 303.15 K and perfluorodecalin + 1-hexene + hexane at 288.15 and 298.15 K are reported. The experimental results are compared with values predicted from the NRTL, the UNIQUAC and the UNIFAC models.

Introduction

Following our experimental determination of binary solubilities (1) and liquid-liquid equilibria for some multicomponent perfluorodecalin + hydrocarbon systems (2), this paper reports the results of measurements on liquid-liquid equilibria for quaternary and ternary systems containing perfluorodecalin, heptane, 1-hexene, and hexane.

Predictions of equilibrium data for these mixtures were made by using the NRTL and UNIQUAC perfluorodecalin + hydrocarbon parameters obtained from binary data. Hydrocarbon + hydrocarbon parameters were calculated by correlating the ternary data. The results are compared with experimental determinations.

The same calculations were made by using the UNIFAC model. The $\text{CH}_2 + \text{CF}_2$ and $\text{CH}_2\text{CH} + \text{CF}_2$ parameters were obtained from binary data (1, 3).

Experimental Section

The experimental work was carried out by using a thermostated miniature cell similar to that described by Soares et al.

(4). Temperature was controlled within an accuracy of 0.01 K and was measured by a calibrated thermometer (German Government Calibration). The mixtures were stirred with a magnetic stirrer for at least 30 min and allowed to settle during a period of 4 h. The tie lines were obtained by analyzing the compositions of the two conjugate phases in equilibrium, by means of a gas chromatograph (flame ionization detector) connected to an integrator. An 8 ft \times 1/4 in. o.d. stainless steel column with 10% squalane in chromosorb PAW, 80/100 mesh was used. The flow rate of N_2 was 60 mL/min, and the oven temperature was 90 °C. Samples were alternatively withdrawn from the two phases with 1- μL chromatographic syringes (one for each phase) and injected into the chromatograph. Special care was taken with the tie-line determination above room temperature to avoid phase splitting due to cooling, by preheating the syringes.

Calibration curves were obtained by using at least 10 mixtures of known composition of which four to six chromatograms were obtained. Four to six samples of both phases were analyzed to minimize the experimental error. Mole fraction measurements were reproducible to within ± 0.002 .

Perfluorodecalin (Aldrich/Europe, cis + trans mixture, minimum purity 97%), hexane and heptane (Merck, minimum purity 99%), and 1-hexene (Fluka, minimum purity 99%) were used as supplied.

Quaternary tie-line data are presented in Table I. Tables II and III summarize the experimental results obtained for the ternary systems. Figures 1 and 2 represent the perfluorodecalin + heptane + 1-hexene system at 288.15 and 298.15 K, respectively. Both are type II systems. At 303.15 K this system is type I and is represented in Figure 3. Figures 4 and 5

Table I. Experimental Liquid-Liquid Equilibrium Compositions for the Quaternary Perfluorodecalin (1) + Heptane (2) + 1-Hexene (3) + Hexane (4)

T/K	mole fractions							
	x_{11}	x_{21}	x_{31}	x_{41}	x_{12}	x_{22}	x_{32}	x_{42}
288.15	0.6995	0.0377	0.0320	0.2308	0.1097	0.1837	0.0810	0.6256
	0.7295	0.0100	0.0395	0.1310	0.0996	0.3729	0.1376	0.3899
	0.7408	0.1305	0.0305	0.0982	0.0939	0.4846	0.1084	0.3131
	0.7558	0.1412	0.0257	0.0773	0.0909	0.5669	0.0901	0.2521
	0.7665	0.1585	0.0318	0.0432	0.0821	0.6474	0.1101	0.1604
	0.7750	0.1782	0.0199	0.0269	0.0819	0.7211	0.0828	0.1142
	0.7760	0.1708	0.0311	0.0221	0.0803	0.6996	0.1188	0.1013
	0.7250	0.1128	0.1455	0.0167	0.0941	0.3874	0.4534	0.0651
	0.7210	0.0944	0.1043	0.0803	0.0983	0.3201	0.3255	0.2561
	0.7087	0.0836	0.0866	0.1215	0.0998	0.2784	0.2666	0.3552
	0.7270	0.1041	0.0793	0.0896	0.0975	0.3740	0.2467	0.2818
	0.7400	0.1161	0.0887	0.0552	0.0967	0.4110	0.3008	0.1915
	0.7331	0.1752	0.0571	0.0346	0.0905	0.5720	0.2009	0.1366
	0.7525	0.1503	0.0692	0.0280	0.0900	0.5845	0.2085	0.1170
	0.7864	0.1525	0.0442	0.0169	0.0824	0.6861	0.1594	0.0721
	0.7914	0.1312	0.0609	0.0165	0.0835	0.6228	0.2255	0.0682
	298.15	0.5289	0.0646	0.3722	0.0373	0.1721	0.1008	0.6586
0.5152		0.0346	0.3671	0.0831	0.1874	0.1016	0.5812	0.1298
0.5682		0.0783	0.2092	0.1443	0.1740	0.1426	0.3997	0.2837
0.5255		0.0550	0.2214	0.1981	0.2007	0.1248	0.3569	0.3176
0.5678		0.1214	0.1302	0.1806	0.1734	0.2525	0.2387	0.3354
0.5743		0.0980	0.1088	0.2189	0.1732	0.2286	0.2006	0.3976
0.5540		0.0908	0.1004	0.2548	0.1927	0.2049	0.1567	0.4457
0.5378		0.0901	0.1001	0.2720	0.2032	0.2066	0.1570	0.4332
0.5352		0.1023	0.0785	0.2840	0.2094	0.1783	0.1289	0.4834
0.5892		0.1089	0.0577	0.2442	0.1713	0.2483	0.1135	0.4669
0.5992		0.0945	0.0483	0.2580	0.1889	0.2738	0.0858	0.4515
0.5356		0.0908	0.0449	0.3287	0.2024	0.1656	0.0752	0.5568
0.5659		0.1161	0.0321	0.2859	0.1827	0.2241	0.0595	0.5337
0.5845		0.1141	0.0260	0.2754	0.1823	0.2604	0.0495	0.5078
0.7091		0.1836	0.0591	0.0482	0.1245	0.5857	0.1568	0.1330
0.6946		0.2358	0.0387	0.0309	0.1205	0.6849	0.1058	0.0888
0.6559		0.2039	0.0351	0.1051	0.1381	0.5313	0.0833	0.2473
0.6265	0.1695	0.0262	0.1778	0.1389	0.4155	0.0639	0.3817	
0.5864	0.1420	0.0242	0.2474	0.1653	0.3139	0.0495	0.4713	
0.5815	0.1355	0.0197	0.2633	0.1686	0.2934	0.0427	0.4953	

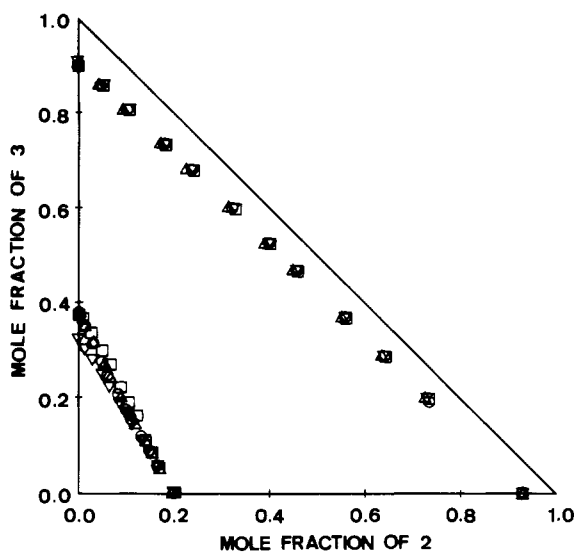


Figure 1. Liquid-liquid equilibrium diagram for perfluorodecalin + heptane + 1-hexene at 288.15 K: (□) experimental data; (○) results of the UNIQUAC equation; (Δ) results of the NRTL equation; (▽) results of the UNIFAC equation.

represent the perfluorodecalin + 1-hexene + hexane system at 288.15 (type II) and 298.15 K (type I), respectively.

Discussion

The prediction of ternary and quaternary liquid-liquid equilibrium data can be made by using the NRTL (5), UNIQUAC (6),

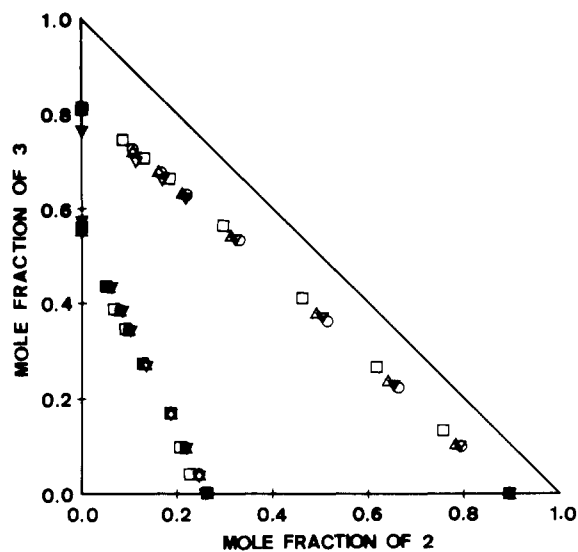


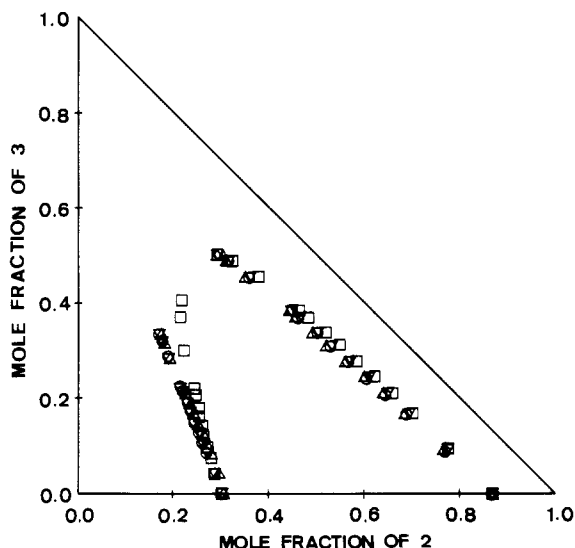
Figure 2. Liquid-liquid equilibrium diagram for perfluorodecalin + heptane + 1-hexene at 298.15 K: (□) experimental data; (○) results of the UNIQUAC equation; (Δ) results of the NRTL equation; (▽) results of the UNIFAC equation.

and UNIFAC (7) models. Agreement between calculated and experimental data is expressed in terms of composition root mean square deviations (RMSD):

$$\text{RMSD} = \left[\frac{\sum_{k=1}^M \sum_{j=1}^N \sum_{i=1}^2 (x_{ijk}^{\text{cal}} - x_{ijk}^{\text{exp}})^2}{2N(M-1)} \right]^{1/2} \quad (1)$$

Table II. Experimental Liquid-Liquid Equilibrium Compositions for the Ternary System Perfluorodecalin (1) + Heptane (2) + 1-Hexene (3)

T/K	mole fractions					
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}
288.15	0.6261	0.0	0.3739	0.0989	0.0	0.9011
	0.6199	0.0140	0.3661	0.0903	0.0522	0.8575
	0.6326	0.0301	0.3373	0.0859	0.1065	0.8076
	0.6481	0.0524	0.2995	0.0803	0.1841	0.7356
	0.6596	0.0701	0.2703	0.0763	0.2421	0.6816
	0.6866	0.0916	0.2218	0.0731	0.3277	0.5992
	0.7016	0.1090	0.1894	0.0738	0.4009	0.5253
	0.7142	0.1229	0.1629	0.0707	0.4609	0.4684
	0.7489	0.1431	0.1100	0.0698	0.5606	0.3696
	0.7581	0.1572	0.0847	0.0683	0.6437	0.2880
	0.7766	0.1728	0.0506	0.0691	0.7312	0.1997
	0.7975	0.2025	0.0	0.0694	0.9306	0.0
	298.15	0.4401	0.0	0.5599	0.1919	0.0
0.5169		0.0501	0.4330	0.1725	0.0859	0.7416
0.5493		0.0666	0.3841	0.1629	0.1331	0.7040
0.5669		0.0904	0.3427	0.1538	0.1860	0.6602
0.6027		0.1272	0.2701	0.1394	0.2964	0.5642
0.6475		0.1861	0.1664	0.1269	0.4627	0.4104
0.6987		0.2052	0.0961	0.1180	0.6174	0.2646
0.7316		0.2290	0.0394	0.1103	0.7574	0.1323
0.7388		0.2612	0.0	0.1037	0.8963	0.0
0.3715		0.2206	0.4079	0.2059	0.2927	0.5014
0.4118		0.2168	0.3714	0.1838	0.3276	0.4886
0.4766		0.2229	0.3005	0.1629	0.3812	0.4559
0.5320		0.2447	0.2233	0.1508	0.4669	0.3823
0.5473	0.2487	0.2040	0.1458	0.4841	0.3701	
0.5654	0.2552	0.1794	0.1421	0.5199	0.3380	
0.5833	0.2557	0.1610	0.1407	0.5478	0.3115	
0.5981	0.2626	0.1393	0.1381	0.5845	0.2774	
0.6160	0.2661	0.1179	0.1360	0.6222	0.2418	
0.6302	0.2735	0.0963	0.1339	0.6585	0.2076	
0.6460	0.2816	0.0724	0.1329	0.7012	0.1659	
0.6702	0.2892	0.0406	0.1314	0.7773	0.0913	
0.6974	0.3026	0.0	0.1319	0.8681	0.0	

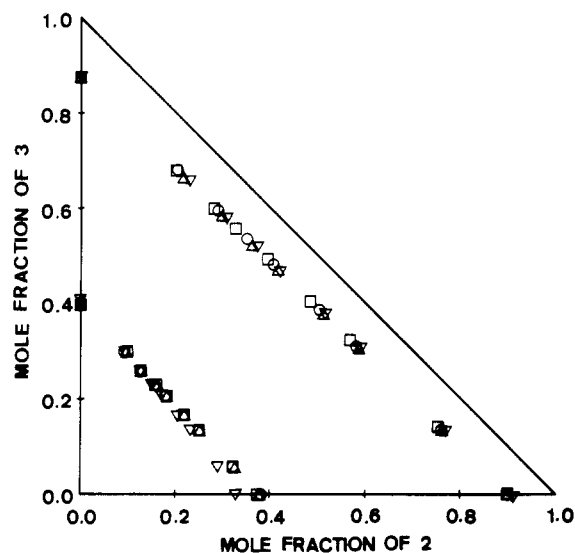
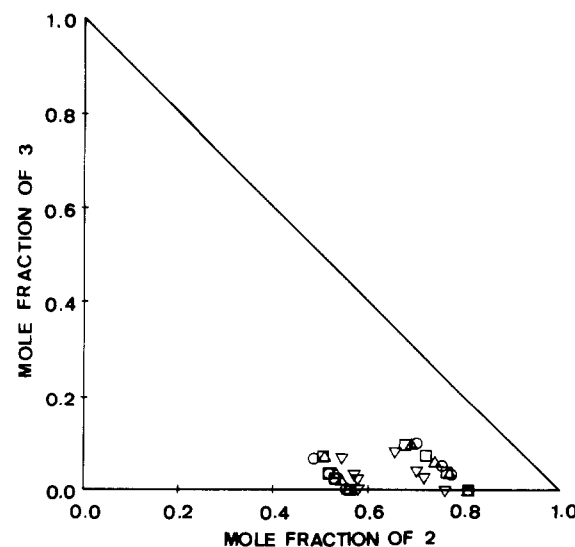
**Figure 3.** Liquid-liquid equilibrium diagram for perfluorodecalin + heptane + 1-hexene at 303.15 K: (□) experimental data; (○) results of the UNIQUAC equation; (△) results of the NRTL equation; (▽) results of the UNIFAC equation.

NRTL and UNIQUAC Equations. Binary NRTL and UNIQUAC parameters were determined by using two alternative approaches.

Method A: ternary data were directly correlated, the number of adjusted parameters was varied from 2 to 6, and α_{ij} (NRTL equation) was kept constant. The values used for the parameter α_{ij} for the perfluorodecalin + hydrocarbon binaries were the recommended values (1, 3). For the hydrocarbon + hydrocarbon binaries, we used the value 0.3, according to Renon and Prausnitz (5).

Table III. Experimental Liquid-Liquid Equilibrium Compositions for the Ternary System Perfluorodecalin (1) + 1-Hexene (2) + Hexane (3)

T/K	mole fractions						
	x_{11}	x_{21}	x_{31}	x_{12}	x_{22}	x_{32}	
288.15	0.6261	0.3739	0.0	0.0989	0.9011	0.0	
	0.6181	0.3244	0.0575	0.1020	0.7533	0.1447	
	0.6173	0.2496	0.1331	0.1081	0.5679	0.3240	
	0.6155	0.2193	0.1652	0.1103	0.4844	0.4043	
	0.6120	0.1813	0.2067	0.1112	0.3972	0.4916	
	0.6113	0.1590	0.2297	0.1145	0.3271	0.5584	
	0.6143	0.1272	0.2585	0.1163	0.2812	0.6025	
	0.6057	0.0988	0.2955	0.1185	0.1998	0.6817	
	0.6059	0.0	0.3941	0.1253	0.0	0.8747	
	0.298.15	0.4401	0.5599	0.0	0.1919	0.8081	0.0
	0.4500	0.5284	0.0216	0.1996	0.7624	0.0380	
	0.4500	0.5161	0.0339	0.2097	0.7193	0.0710	
	0.4291	0.5031	0.0678	0.2269	0.6764	0.0967	

**Figure 4.** Liquid-liquid equilibrium diagram for perfluorodecalin + 1-hexene + hexane at 288.15 K: (□) experimental data; (○) results of the UNIQUAC equation; (△) results of the NRTL equation; (▽) results of the UNIFAC equation.**Figure 5.** Liquid-liquid equilibrium diagram for perfluorodecalin + 1-hexene + hexane at 298.15 K: (□) experimental data; (○) results of the UNIQUAC equation; (△) results of the NRTL equation; (▽) results of the UNIFAC equation.

drocarbon binaries, we used the value 0.3, according to Renon and Prausnitz (5).

Method B: for the perfluorodecalin + hydrocarbon binaries, the linear temperature dependence of parameters, obtained

Table IV. Recommended Values for the NRTL and UNIQUAC Parameters at 288.15, 298.15, and 303.15 K

system	T/K	NRTL			UNIQUAC	
		α_{12}	b_{12}/K	b_{21}/K	c_{12}/K	c_{21}/K
perfluorodecalin + hexane	288.15	0.4	369.6	651.1	152.8	-11.85
	298.15	0.4	318.6	585.7	162.3	-26.64
	303.15	0.4	291.6	550.2	167.1	-34.08
perfluorodecalin + heptane	288.15	0.3	337.6	678.7	158.7	-8.34
	289.15	0.3	306.6	640.3	162.0	-17.33
	303.15	0.3	290.1	619.3	163.6	-21.92
perfluorodecalin + 1-hexene	288.15	0.4	362.8	688.7	158.2	-8.24
	289.15	0.4	295.8	640.2	154.8	-13.98
	303.15	0.4	260.4	614.5	153.0	-17.07

Table V. RMSD ($\times 10^2$) between Calculated and Experimental Values^a

system	T/K	type	NRTL		UNIQUAC		UNIFAC
			A	B	A	B	
perfluorodecalin + heptane + 1-hexene	288.15	II	1.13	1.74	0.84	0.96	3.10
	298.15	II	1.18	1.24	2.38	2.49	2.50
	303.15	I	1.70	1.64	1.52	1.66	3.33
perfluorodecalin + 1-hexene + hexane	288.15	II	1.40	1.40	0.71	0.80	1.71
	298.15	I	1.28	1.28	1.39	1.39	4.19
perfluorodecalin + heptane + 1-hexene + hexane	288.15	III	1.49	1.32	2.02	1.94	2.06
	298.15	II	1.17	1.19	1.33	1.35	1.60

^aA = RMSD obtained by using method A; B = RMSD obtained by using the method B.

from the correlation of binary solubility data (1, 3) was used; hydrocarbon + hydrocarbon parameters were calculated by adjusting ternary tie-line data.

Binary parameters from ternary data were calculated by using the Nelder-Mead method for the minimization of the following objective functions:

$$F1 = \sum_{k=1}^M \sum_{i=1}^N [\ln(\gamma_{i1}/\gamma_{i2}) - \ln(x_{i2}/x_{i1})]_k^2 \quad (2)$$

$$F2 = \sum_{k=1}^M \sum_{i=1}^N \sum_{j=1}^2 (x_{ijk}^{\text{cal}} - x_{ijk}^{\text{exp}})^2 \quad (3)$$

with $3M > L$, M being the available number of tie lines, N is the number of components, and L is the number of parameters.

The NRTL and UNIQUAC parameters recommended for the perfluorodecalin + hydrocarbon binaries are presented in Table IV.

Table V shows the values of RMSD between experimental and calculated compositions.

UNIFAC Model (Modified). UNIFAC group parameters for the interactions $\text{CH}_2 + \text{CF}_2$ and $\text{CH}_2=\text{CH} + \text{CF}_2$ were obtained from mutual solubility data (1, 3). We consider these parameters dependent on the temperature and the number of carbon atoms of the hydrocarbon. For example, in the mixture perfluorodecalin + heptane + 1-hexene we have the interactions $\text{CH}_2 + \text{CF}_2$ (6) and $\text{CH}_2 + \text{CF}_2$ (7).

Table V also includes the values of RMSD obtained by using the UNIFAC model.

Conclusions

The experimental results were correlated in terms of NRTL, UNIQUAC, and UNIFAC equations. The results are represented in Figures 1-5. In general, these models represent the binodal curves correctly for type II systems. Some deviations were found in the direction of the tie lines. The prediction results are not so good for type I systems.

Looking at the results in Table V, we can see that, with slightly less accuracy, relative to the results obtained from direct correlation of data of each individual ternary system (method A), it is possible to obtain a set of NRTL and UNIQUAC parameters applicable to all multicomponent mixtures of perfluorodecalin and hydrocarbons (method B).

The RMSD values between experimental and calculated compositions are, in general, larger for the UNIFAC method than for the NRTL and UNIQUAC equations.

List of Symbols

A, B = method of correlation of ternary data (Table V)

b_{ij} = NRTL parameter/K

c_{ij} = UNIQUAC parameter/K

F1, F2 = objective functions

x_{ij} = molar fraction of component i in phase j

RMSD = root mean square deviation

Greek Letters

α_{ij} = nonaleatory NRTL parameter

γ_i = activity coefficient of component i

Registry No. $\text{H}_3\text{C}(\text{CH}_2)_5\text{CH}_3$, 142-82-5; $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{CH}_3$, 592-41-6; $\text{H}_3\text{C}(\text{CH}_2)_4\text{CH}_3$, 110-54-3; perfluorodecalin, 306-94-5.

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