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Liquid−Liquid Equilibria of (Limonene + Linalool + Ethylene Glycol or Diethylene Glycol or Triethylene Glycol or 1,2-Propylene Glycol) Ternary Systems

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Liquid–liquid equilibrium (LLE) data of the solubility (binodal) curves and tie-line compositions were examined for mixtures of (limonene (1) + linalool (2) + ethylene glycol or diethylene glycol or triethylene glycol or 1,2-propylene glycol (3)) at 298.15 K and 101.3 ± 0.7 kPa. The relative mutual solubility of linalool is higher in the limonene layers than in the ethylene glycol or diethylene glycol or triethylene glycol or 1,2-propylene glycol layers. The reliability of the experimental tie-line data was confirmed by using the Othmer−Tobias correlation. The LLE data of the ternary systems was predicted by the UNIFAC method. Distribution coefficients and separation factors were evaluated for the immiscibility region.

Introduction

Citrus oil is used in a wide variety of applications in major industries such as the flavor, food, cosmetic, pharmaceutical, and chemical industries. They are obtained from the small glands contained in the colored portion of the citrus peel. Citrus oil is an essential oil, the two main components of which are the terpene hydrocarbon, limonene, and the oxygenated terpenoid, linalool (Figure 1). Essential oils, representing the essences or odor constituents of plants, are usually purified to remove the large content of hydrocarbon terpenes present in the oil and, as a consequence, to concentrate the oxygenated compounds, which represent the flavor fraction. This is conventionally processed by distillation or solvent extraction. The solvent extraction method reduces energy consumption and avoids thermal degradation of valuable components.[1–3]

Unfortunately, the study of the solvent extraction technique is limited by the lack of data on the thermodynamic behavior of systems containing terpenes, oxygenated compounds, and solvent. Liquid–liquid equilibrium (LLE) data of the system limonene + ethanol + water from (293.15 to 323.15) K,[4] linalool + ethanol + water,[5] limonene + linalool + diethylene glycol,[6] limonene + linalool + 2-aminoethanol[7] and limonene + linalool + (1,2-propanediol or 1,3 propanediol)[8] and water + ethanol + citral and water + ethanol + limonene at 293 K[9] are available in the literature.

The LLE data were predicted by the UNIFAC (universal functional group activity coefficient) method.[10] The UNIFAC method is used to predict the activity coefficients, γ_i. In LLE, the mole fractions x_i^{E}, x_i^{R} of conjugate phases can be calculated by using the following equations

$$(\gamma_i x_i)^{\mathrm{E}} = (\gamma_i x_i)^{\mathrm{R}} \tag{1}$$

where γ_i^{E} and γ_i^{R} are the corresponding activity coefficients of component i in extract and raffinate phases. The interaction parameters between each main group are used to calculate activity coefficients of component i. The values of the UNIFAC parameters for LLE predictions were taken from a UNIFAC table.[11]

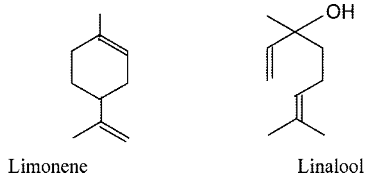

Figure 1. Structures of limonene and linalool.

We undertook a systematic study of the phase equilibrium established between limonene and linalool (two main components of citrus essential oil) and solvents to extract linalool from the citrus essential oil. The common property of these solvents is that they have polar groups. In this study, LLE results were reported for the four ternary systems, (limonene + linalool + ethylene glycol), (limonene + linalool + diethylene glycol), (limonene + linalool + triethylene glycol), and (limonene + linalool + 1,2 propylene glycol) at $T = 298.15$ K.

Experimental

Materials. All chemicals used were chromatography-grade products supplied by Merck with nominal purities of 0.99 mass fraction for ethylene glycol, 0.99 mass fraction for diethylene glycol, 0.99 mass fraction for triethylene glycol, 0.99 mass fraction for 1,2-propylene glycol, 0.97 mass fraction for limonene, and 0.97 mass fraction for linalool. These purities were verified by gas chromatography, and the chemicals were used without further purification.

Refractive indices were measured with an Anton Paar refractometer (RXA 170 model) with a stated accuracy of $\pm 5 \cdot 10^{-5}$. Densities were measured with an Anton Paar densimeter (DMA 4500 model). Boiling point measurements were obtained by using a Fischer boiling point apparatus. The estimated uncertainties in the density and boiling point measurements were $\pm 1 \cdot 10^{-2}$ kg·m^{-3} and ± 0.1 K, respectively. The measured physical properties are listed in Table 1, along with literature values.[12]

Procedure. The solubility curves were determined by the cloud point method in an equilibrium glass cell with a water jacket to maintain isothermal conditions. The temperature in the cell was kept constant by circulating water from a water bath (NUVE, BS 302 model), which was equipped with a

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Table 1. Physical Properties of the Pure Components at $T = 293.15$ K and $p = 101.325$ kPa[12]

	$\rho/(\mathrm{kg \cdot m^{-3}})$		n_D		T_b/K	
compound	exptl	lit.	exptl	lit.	exptl	lit.
limonene	840.24[a]	840.2[a]	1.47274[b]	1.4727[b]	451.3	451
linalool	870.04[c]	870.0[c]	1.46272	1.4627	471.1	471
ethylene glycol	1115.52	1115.5	1.43184	1.4318	470.1	470.3
diethylene glycol	1119.74[c]	1119.7[c]	1.44724	1.4472	521.9	521.8
triethylene glycol	1127.43[c]	1127.4[c]	1.45314	1.4531	557.6	558
1,2-propylene glycol	1032.83	1032.8	1.43143	1.4314	462.4	462

[a] 294 K. [b] 292 K. [c] 288 K.

Table 2. Experimental Solubility Curve Data for (Limonene + Linalool + Glycol) Ternary Systems

x_1	x_2	x_3
{Limonene (1) + Linalool (2) + Ethylene Glycol (3)}		
0.956	0.020	0.024
0.912	0.054	0.034
0.896	0.066	0.038
0.880	0.082	0.038
0.860	0.101	0.039
0.106	0.187	0.707
0.073	0.153	0.774
0.065	0.118	0.817
0.040	0.102	0.858
0.031	0.031	0.938
0.956	0.020	0.024
{Limonene (1) + Linalool (2) + Diethylene Glycol (3)}		
0.978	0.000	0.022
0.848	0.104	0.048
0.686	0.201	0.113
0.599	0.230	0.171
0.421	0.253	0.326
0.335	0.248	0.417
0.160	0.210	0.630
0.106	0.187	0.707
0.047	0.107	0.846
0.015	0.000	0.985
{Limonene (1) + Linalool (2) + Triethylene Glycol (3)}		
0.966	0.000	0.034
0.892	0.072	0.036
0.752	0.168	0.080
0.598	0.229	0.173
0.425	0.254	0.321
0.283	0.247	0.470
0.121	0.172	0.707
0.030	0.076	0.894
0.003	0.000	0.997
{Limonene (1) + Linalool (2) + 1,2-Propylene Glycol (3)}		
0.962	0.000	0.038
0.820	0.101	0.079
0.617	0.182	0.201
0.516	0.192	0.292
0.403	0.192	0.405
0.310	0.181	0.509
0.280	0.180	0.540
0.229	0.167	0.604
0.145	0.148	0.707
0.087	0.113	0.800
0.031	0.062	0.907
0.014	0.000	0.986

temperature controller capable of maintaining the temperature within ± 0.1 K. The major central part of the solubility curves was obtained by titrating heterogeneous mixtures of the limonene + glycol with linalool until the turbidity had disappeared. For the limonene-side and glycol-side, binary mixtures of either (limonene + linalool) or (glycol + linalool) were titrated against the third component until the transition from homogeneity to heterogeneity was observed. All mixtures were prepared by weighing by means of Sartorious CP224S with an accuracy of $\pm 1 \cdot 10^{-7}$ kg.

Mutual solubility values of the binary mixture (limonene + glycol) were measured using the method based on the detection of the cloud point. The transition point between the homogeneous and heterogeneous zones was determined visually. The reliability of the method depends on the precision of the Metrohm microburette, with an accuracy of $\pm 3 \cdot 10^{-9}$ m^3, and is limited by the visual inspection of the transition across the apparatus. The accuracy of the visual inspection of the transition is achieved by waiting for about 5 min in the transition point and observing the heterogeneity. All visual experiments were repeated at least three times to acquire high accuracy.

End-point determinations of the tie-lines were carried out by the independent analysis of the conjugate phases that were regarded as being in equilibrium. Mixtures of known masses of limonene, linalool, and glycol lying within the heterogeneous gap were introduced into the extraction cell and were stirred vigorously for at least 4 h and then left for 6 h (the time necessary to attain equilibrium was established in preliminary experiments) to settle down into limonene and glycol layers.

Analysis. The liquid samples were analyzed by a gas chromatograph (HP 6890 model) equipped with a flame ionization detector (FID). An HP-Innowax polyethylene glycol capillary column (30 m × 0.32 mm × 0.5 μm) for an FID was utilized to separate components of samples at programmed oven programs suitable for each ternary. The detector temperature was kept at $T = 473.15$ K, while the injection port temperature was held at $T = 543.15$ K. Injections were performed on the split 70:1 mode. Nitrogen was used as a carrier gas with a flow rate of 2.6 cm$^3 \cdot$min^{-1}. Injection volumes of the liquid samples were 0.3 μL. The greatest errors in the determination of mole fraction composition using the calibration curves were ± 0.002 in the limonene-rich phase and ± 0.002 in the glycol-rich phase.

Results and Discussion

The compositions of the mixture on the binodal curve, as well as the mutual binary solubility of limonene and glycol at 298.15 K, were given in Table 2, in which x_i denotes the mole fraction of the ith component. Table 3 shows the experimental tie-line compositions of the equilibrium phases, for which x_{i1} and x_{i3} refer to the mole fractions of the ith component in the limonene and glycol phases, respectively. The binodal curves and tie-lines are shown in Figures 2 to 5. Figures 2 to 5 show that the area of the two-phase heterogeneous region changes in the order of 1,2-propylene glycol < triethylene glycol < diethylene glycol < ethylene glycol. The slopes of the tie-lines obtained in this work show that linalool is more soluble in the limonene than in glycols.

Distribution coefficients, d_i, for limonene ($i = 1$) and linalool ($i = 2$) and separation factors, s, were calculated as follows

Table 3. Experimental Tie-Line Data of (Limonene + Linalool + Glycol) Ternary Systems

limonene-rich phase (mole fraction)			glycol-rich phase (mole fraction)		
x_{11}	x_{21}	x_{31}	x_{13}	x_{23}	x_{33}
{Limonene (1) + Linalool (2) + Ethylene Glycol (3)}					
0.891	0.067	0.042	0.005	0.008	0.987
0.828	0.093	0.079	0.006	0.009	0.985
0.806	0.131	0.063	0.005	0.010	0.985
0.739	0.179	0.082	0.005	0.012	0.983
0.678	0.223	0.099	0.006	0.013	0.981
0.629	0.251	0.120	0.006	0.015	0.979
0.578	0.291	0.131	0.006	0.017	0.977
0.526	0.316	0.158	0.007	0.019	0.974
{Limonene (1) + Linalool (2) + Diethylene Glycol (3)}					
0.938	0.031	0.031	0.024	0.020	0.956
0.859	0.101	0.040	0.033	0.054	0.913
0.817	0.118	0.065	0.038	0.066	0.896
0.774	0.153	0.073	0.038	0.082	0.880
0.708	0.186	0.106	0.038	0.101	0.861
{Limonene (1) + Linalool (2) + Triethylene Glycol (3)}					
0.926	0.039	0.035	0.009	0.019	0.972
0.867	0.096	0.037	0.024	0.058	0.918
0.803	0.136	0.061	0.049	0.089	0.862
0.740	0.184	0.076	0.053	0.113	0.834
{Limonene (1) + Linalool (2) + 1,2-Propylene Glycol (3)}					
0.921	0.033	0.046	0.017	0.014	0.969
0.849	0.077	0.074	0.023	0.025	0.952
0.771	0.127	0.102	0.025	0.050	0.925
0.666	0.161	0.173	0.030	0.062	0.908

$$d_i = x_{i3}/x_{i1} \tag{2}$$

$$s = \frac{\text{distribution coefficient of linalool}}{\text{distribution coefficient of limonene}} = (x_{23}/x_{21})/(x_{13}/x_{11}) \tag{3}$$

where x_{23} and x_{21} are the mole fractions of linalool in glycol-rich and limonene-rich phases, respectively, and x_{13} and x_{11} are the limonene mole fractions in glycol-rich and limonene-rich phases, respectively.

The distribution coefficients and separation factors for each glycol are given in Table 4. The effectiveness of extraction of linalool through solvent is given by its separation factor, which is an indication of the ability of solvent to separate linalool from limonene. This quantity is found to be greater than 1 (separation factors varying between 4.82 and 50.94) for the systems reported here, which means that extractions of linalool by the glycols are possible. The separation factors and distribution coefficients are not constant over the completely two-phase region. The extracting power of the glycols is shown in Figures 6 and 7.

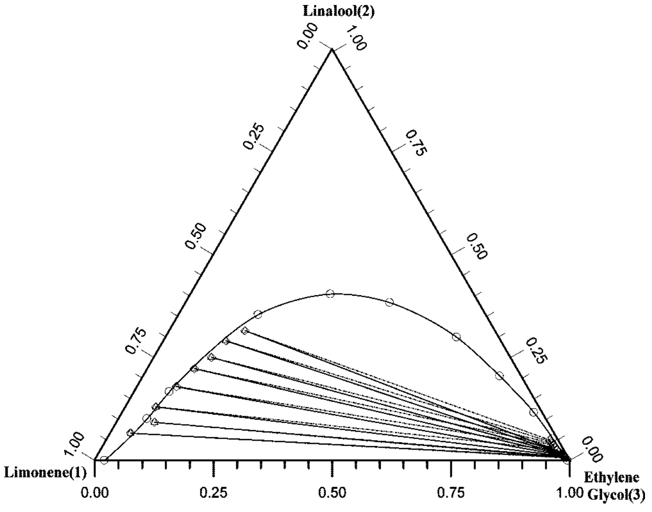

Figure 2. Ternary diagram for LLE of {limonene (1) + linalool (2) + ethylene glycol (3)} at T = 298.15 K: -O-, experimental solubility curve; -Δ-, experimental tie-lines; --◊--, calculated (UNIFAC) tie-lines.

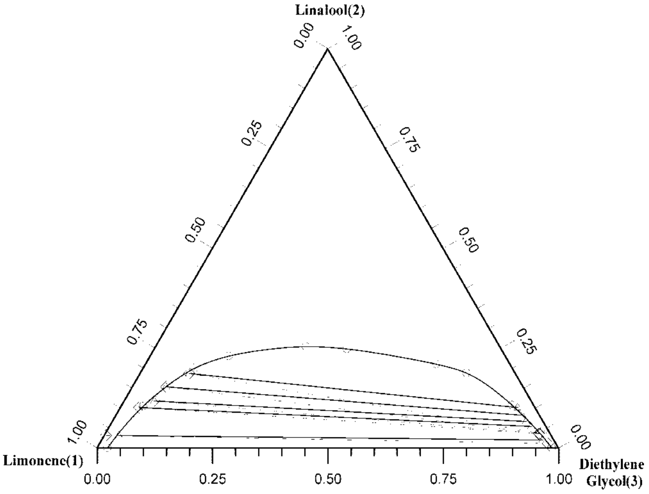

Figure 3. Ternary diagram for LLE of {limonene (1) + linalool (2) + diethylene glycol (3)} at T = 298.15 K: -O-, experimental solubility curve; -Δ-, experimental tie-lines; --◊--, calculated (UNIFAC) tie-lines.

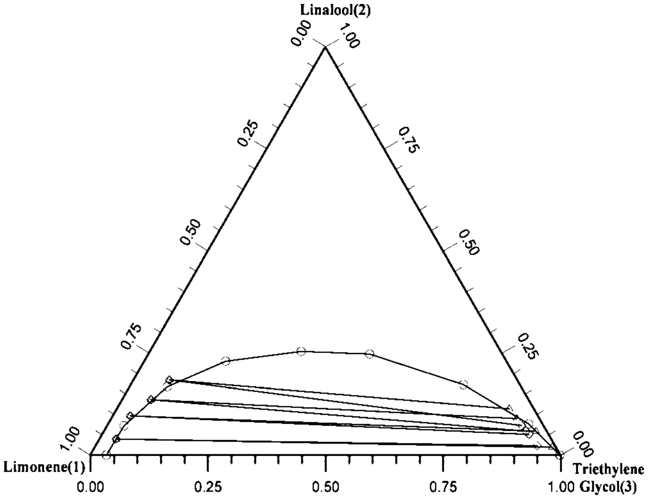

Figure 4. Ternary diagram for LLE of {limonene (1) + linalool (2) + triethylene glycol (3)} at T = 298.15 K: -O-, experimental solubility curve; -Δ-, experimental tie-lines; --◊--, calculated (UNIFAC) tie-lines.

The reliability of experimentally measured tie-line data can be ascertained by applying the Othmer–Tobias correlation[13] for each solvent as shown in the following equation

$$\ln(1 - x_{11})/x_{11} = a + b \ln(1 - x_{33})/x_{33} \tag{4}$$

where x_{11} is the mole fraction of limonene in the limonene-rich phase; x_{33} is the mole fraction of the glycol in the glycol-rich phase; and a and b are the constant and slope of eq 4.

Othmer–Tobias plots were constructed of the $\ln\{(1 - x_{11})/x_{11}\}$ vs $\ln\{(1 - x_{33})/x_{33}\}$. The correlations are shown in Figure 8 at T = 298.15 K. The fact that the correlation is linear indicates the degree of consistency of the related data.

The equilibrium data of the ternary systems were predicted by UNIFAC and a method using the interaction parameters of C, CH, CH_2, CH_3, CH=C, CH_2=CH, CH_2=C, OH, and CH_2O functional groups obtained by Reid et al.[11] The calculated tie-lines (dashed lines) were presented in Figures 2 to 5.

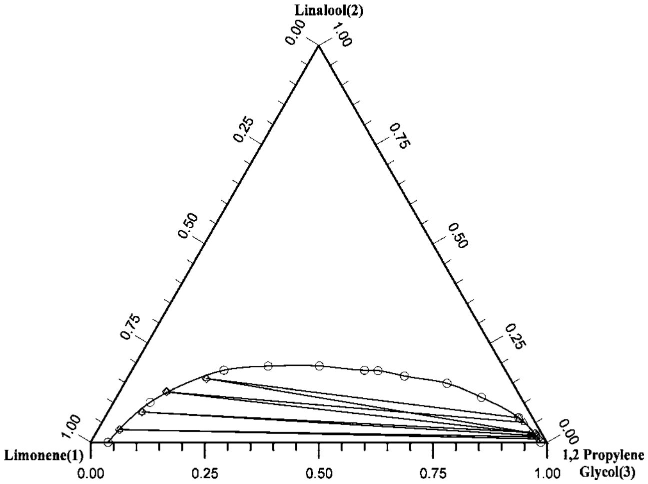

Figure 5. Ternary diagram for LLE of {limonene (1) + linalool (2) + 1,2-propylene glycol (3)} at $T = 298.15$ K: -○-, experimental solubility curve; -Δ-, experimental tie-lines; --◇--, calculated (UNIFAC) tie-lines.

Table 4. Distribution Coefficients for Limonene (d_1) and Linalool (d_2) and Separation Factors (s)

d_1	d_2	s
{Limonene (1) + Linalool (2) + Ethylene Glycol (3)}		
0.006	0.114	19.94
0.007	0.095	13.29
0.006	0.080	12.60
0.007	0.067	9.32
0.008	0.060	7.10
0.009	0.062	6.56
0.010	0.059	5.70
0.013	0.061	4.82
{Limonene (1) + Linalool (2) + Diethylene Glycol (3)}		
0.026	0.643	24.72
0.038	0.529	13.81
0.046	0.563	12.21
0.049	0.534	10.83
0.054	0.542	9.96
{Limonene (1) + Linalool (2) + Triethylene Glycol (3)}		
0.010	0.490	50.94
0.027	0.607	22.12
0.061	0.658	10.83
0.072	0.616	8.60
{Limonene (1) + Linalool (2) + 1,2-Propylene glycol (3)}		
0.018	0.428	23.87
0.027	0.330	12.42
0.032	0.392	12.27
0.045	0.385	8.60

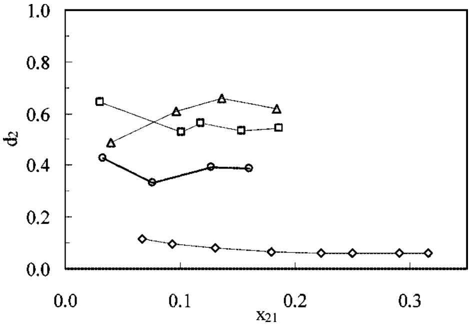

Figure 6. Distribution coefficient of linalool, d_2, plotted against the mole fraction of linalool in the limonene phase, x_{21}: -◇-, ethylene glycol; -□-, diethylene glycol; -Δ-, triethylene glycol; -○-, 1,2-propylene glycol.

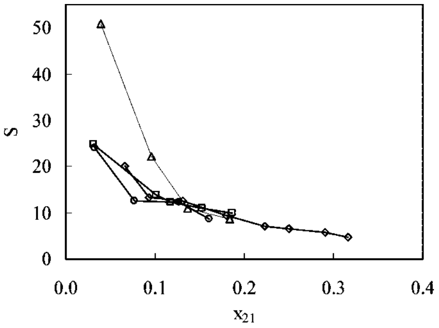

Figure 7. Separation factor, s, plotted against the mole fraction of linalool in the limonene phase, x_{21}: -◇-, ethylene glycol; -□-, diethylene glycol; -Δ-, triethylene glycol; -○-, 1,2-propylene glycol.

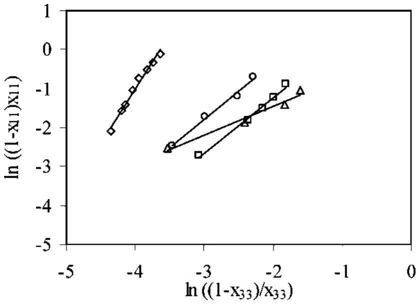

Figure 8. Othmer–Tobias plots of the {limonene (1) + linalool (2) + glycol (3)} ternary systems at $T = 298.15$ K: -◇-, ethylene glycol; -□-, diethylene glycol; -Δ-, triethylene glycol; -○-, 1,2-propylene glycol.

The quality of prediction is evaluated with the residual function (F) calculated from the difference between the experimental data and the predictions of the UNIFAC method for each ternary system according to the following equation

$$F = \left\{ \sum_k \min \left[\sum_i \sum_j (x_{i,\text{exptl}} - x_{i,\text{calcd}})^2 \right] / 6n \right\}^{1/2} \qquad (5)$$

where n is the number of tie-lines; $x_{i,\text{exptl}}$ is the experimental mole fraction; $x_{i,\text{calcd}}$ is the calculated mole fraction of component i; j refer to phases; and $k = 1, 2, 3, 4. . .n$ (tie-lines). The UNIFAC method correlated the experimental data for the systems with ethylene glycol, diethylene glycol, triethylene glycol, and 1,2-propylene glycol at $T = 298.15$ K with F values of 0.0278, 0.0558, 0.0330, and 0.0305, respectively.

Arce et al. studied tie-lines of (limonene + linalool + diethylene glycol) and (limonene + linalool + 1,2-propandiol) systems.[6,8] They predicted LLE using UNIFAC parameters of Magnussen et al.[14] with F values of 0.060571 and 0.1132, respectively. We studied tie-lines of the same systems at 298.15 K and found similar experimental tie-line data. In addition, we also studied solubility curves of the same systems. LLE data were predicted using UNIFAC parameters of Reid et al.[11] The calculated results fitted the LLE data of (limonene + linalool + diethylene glycol), and (limonene + linalool + 1,2-propandiol) systems are slightly better than the results of Arce et al.[6,8] with F values of 0.0558 and 0.0305.

Selectivity diagrams on a solvent-free basis are obtained by plotting $x_{23}/(x_{23} + x_{13})$ vs $x_{21}/(x_{21} + x_{11})$ for each glycol in Figure 9. The selectivities of the ternary systems were found to be similar.

Conclusion

The LLE data for the ternary systems of (limonene + linalool + ethylene glycol), (limonene + linalool + diethylene glycol), (limonene + linalool + triethylene glycol), and (limonene + linalool + 1,2-propylene glycol) at $T = 298.15$ K are reported. The LLE data were also predicted by the UNIFAC method, which has not fitted the experimental data quantitatively, but it agrees qualitatively. It is concluded that the glycols used in this

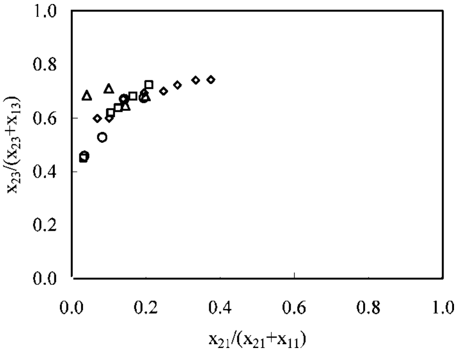

Figure 9. Selectivity diagram of the {limonene (1) + linalool (2) + glycol (3)} ternary systems at $T = 298.15$ K: -◇-, ethylene glycol; -□-, diethylene glycol; -Δ-, triethylene glycol; -○-, 1,2-propylene glycol.

study may serve as suitable solvents to extract linalool from its dilute limonene solutions since they show slight solubility in limonene. The tie-lines in Figures 2 and 4 show that linalool is more readily soluble in the limonene-rich phase than in the glycol-rich phase. It is apparent from the distribution and selectivity data (Table 4) that the separation of linalool from limonene by extraction with the glycols is feasible. Another noteworthy observation is that the complete break of conjugate phases was not hindered by density, viscosity, and/or interfacial tension related phenomena during the settling process.

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