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Solid−Liquid Equilibria, Excess Molar Volumes, and Molar Refractivity Deviations for Extractive Solvents of Molybdenum

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The solid−liquid equilibrium (SLE) for selective solvents, used in the extraction of molybdenum (Mo) from acidic media of Mo ore, has been determined by visual method. The measured SLE data of the systems, trioctylamine (TOA) + 1-octanol, TOA + 1-decanol, and TOA + tributylphosphate (TBP), were correlated by the nonrandom two-liquid (NRTL) and universal quasi-chemical (UNIQUAC) equations and also compared with the calculated values by the modified universal functional activity coefficient (UNIFAC) equation. In addition, the excess molar volumes (V^E) and molar refractivity deviations (ΔR) data at 298.15 K were determined for the same components. These binary V^E and ΔR data were correlated with the Redlich−Kister equation. Furthermore, the ternary V^E and ΔR for the systems TOA + TBP + 1-octanol, TOA + 1-octanol + 1-decanol, TOA + TBP + 1-decanol, and TBP + 1-octanol + 1-decanol are calculated from the correlated binary Redlich−Kister parameters using the Radojkovič equation.

Introduction

Molybdenum (Mo) is a strategic metal and is industrially used in high-pressure and temperature-resistant greases between metals, as pigments, and as catalysts. It is also a necessary element for the human body and plants. Therefore, the extraction and purification processes of Mo are very important. The extraction of Mo from acidic media was usually carried out by solvent extraction, and trioctylamine (TOA), tributylphosphate (TBP), 1-octanol, and 1-decanol are usually used in the Mo extraction process, separately or together as a solvent or modifier.[1−4]

The solvent effect for developing an extraction process is very important, and much more attention should be paid to solvent mixtures. Solvent−solvent interactions produced in solvent mixtures can affect the solute−solvent interactions. Therefore, we need to study thermodynamic properties between related solvents. Besides, the phase equilibria between solvent and modifiers are very important for a study of the solvent recovery process and also for the development of clean technology. Crystallization could be used as an energy-saving process for the separation of Mo extractive solvents, which have relatively high boiling points.[5−7] The solid−liquid equilibrium (SLE) is a basic phase behavior for the development of the crystallization process. The excess properties are used to understand molecular interactions of a nonideal mixture. Experimental data on macroscopic properties such as excess molar volumes (V^E), viscosity deviation, and molar refractivity deviations (ΔR) often provide information for the understanding of the molecular interactions. In addition, V^E is very conveniently used because they are directly measured and just same as the volume change of mixing and can be related to the activity coefficient. On the other hand, ΔR was published very infrequently in the literature.

In this work, therefore, the SLE for the binary systems, TOA + 1-octanol, TOA + 1-decanol, and TOA + TBP, was determined by the visual method.[5] These SLE data can be used to develop a crystallization process for recycling the solvent because they are not available in the literature as far as we know.[8] The measured SLE data were correlated with the nonrandom two-liquid (NRTL)[9] and universal quasi-chemical (UNIQUAC)[10] equations and compared with the calculated values by the modified universal functional activity coefficient (UNIFAC).[11] In addition, V^E and ΔR at 298.15 K are reported for the following binary systems: TOA + 1-octanol, TOA + 1-decanol, TOA + TBP, TBP + 1-octanol, TBP + 1-decanol, and 1-octanol + 1-decanol. These binary V^E and ΔR data were correlated with the Redlich−Kister polynomial.[12] Because of the lack of ternary mixture properties, the ternary V^E and ΔR were calculated by the Radojkovič equation[13] using the correlated Redlich−Kister parameters for the following systems: TOA + TBP + 1-octanol, TOA + 1-octanol + 1-decanol, TOA + TBP + 1-decanol, and TBP + 1-octanol + 1-decanol.

Experimental Section

Materials. All chemicals were supplied from a commercial chemical company. TOA, 1-octanol, and TBP were obtained from Aldrich, while 1-decanol was supplied from Acros. The purity of chemicals was checked by gas chromatography and by comparing the density and refractive index with literature values.[14−17] The purity of the chemicals showed more than 99.9 wt % by gas chromatography. The determined density, refractive index, and melting point of pure components are listed in Table 1 with the literature values and with UNIQUAC parameters.

Apparatus and Procedure. The SLE was measured using a triple jacket glass still, in which the melting process can be observed visually. The melting point of a given composition was determined when the last crystal of mixture component disappears. The measuring apparatus is shown in Figure 1. It consists of a glass still, low-temperature thermostat, and temperature measuring system. The exterior vacuum jacket of

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Table 1. Purity and Physical Properties of Chemicals Used in This Work

	$\rho/(\text{g}\cdot\text{cm}^{-3})$ at 298.15 K		refractive index at 298.15 K		T_{fus}/K		$\Delta H_{\text{fus}}{}^{a}$	UNIQUAC	
chemicals	present study	lit. value[a]	present study	lit. value	present study	lit. value[a]	$\text{J}\cdot\text{mol}^{-1}$	r^{a}	q^{a}
TOA	0.80746	0.8074[b]	1.44758	1.4476[b]	238.73	238.65	27532.0	17.1510	13.9760
1-octanol	0.82176	0.8215[c]	1.42754	1.4276[d]	257.85	257.70	23689.8	6.1519	5.2120
1-decanol	0.82659	0.8267[c]	1.43541	1.4353[d]	280.19	280.05	37630.5	7.5007	6.2920
TBP	0.97269	0.9727[a]	1.42252	1.4224[e]	194.31	194.15	15740.0	9.5046	8.1240

[a] Ref 8. [b] Ref 16. [c] Ref 17. [d] Ref 14. [e] Ref 15.

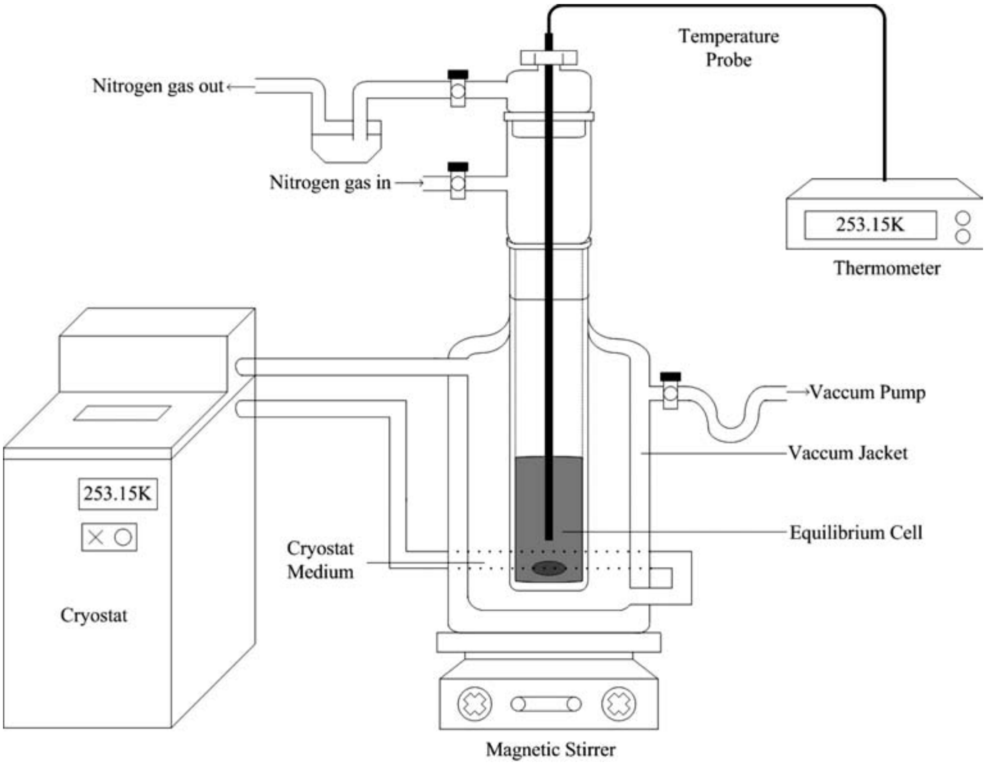

Figure 1. Schematic diagram of the SLE experimental system.

the glass still prevents the freezing of water in the air on the glass surface at low temperatures to make visual observations. The cryostat medium flows through the central jacket to insulate the equilibrium cell via the contact medium. A nitrogen atmosphere in the equilibrium cell is for dehumidification. The temperature was determined with a digital thermometer (ASL F250, U.K.). The accuracy of the melting temperature was determined to be ± 0.02 K, and the estimated uncertainty of the mole fraction was less than $\pm\ 1\cdot10^{-4}$.

The densities were measured using a digital vibrating glass tube densimeter (Anton Paar, model DMA 5000, Austria). The uncertainty of the density measurement was less than $\pm\ 5\cdot10^{-6}$ $\text{g}\cdot\text{cm}^{-3}$ within the range of (0 to 3) $\text{g}\cdot\text{cm}^{-3}$, and the accuracy of temperature was ± 0.01 K. Before each series of measurements, the apparatus was calibrated with doubly distilled water and dried air. Samples were prepared in an about 5 mL glass vial by mass using a microbalance (A&D, HA202, Japan) with a precision of $\pm\ 1\cdot10^{-5}$ g, charging the higher boiling component first to minimize vaporization effects. The estimated uncertainty in the mole fraction of the mixture sample was less than $\pm\ 1\cdot10^{-4}$. Refractive indices (n_{D}) were measured by a digital precision refractometer (KEM, model RA-520N, Japan). The uncertainty of this refractometer is stated by manufacturer as $\pm\ 5\cdot10^{-5}$ within the range from 1.32 to 1.40 and $\pm\ 1\cdot10^{-4}$ within range from 1.40 to 1.58. The experimental procedure is also described in detail elsewhere.[18]

Results and Discussion

Solid−Liquid Equilibrium. At the solid−liquid equilibrium, the fugacity of component i in the liquid phase must be equal to the fugacity of the same component in the solid phase, as in eq 1.

$$f_i^{\text{S}} = f_i^{\text{L}} \tag{1}$$

After some simplification, the following equation is obtained, and it involves the properties of pure solute, such as the enthalpy of fusion, melting temperature, and so forth.[5]

$$\ln(\gamma_i x_i) = -\frac{\Delta H_{\text{fus},i}}{R}\left[\frac{1}{T} - \frac{1}{T_{\text{fus},i}}\right] - \frac{\Delta H_{\text{trs},i}}{R}\left[\frac{1}{T} - \frac{1}{T_{\text{trs},i}}\right] \tag{2}$$

where x_i is the mole fraction in the liquid phase, γ_i the activity coefficient in the liquid phase, $\Delta H_{\text{fus},i}$ the molar enthalpy of fusion, $T_{\text{fus},i}$ the melting temperature, $\Delta H_{\text{trs},i}$ the molar enthalpy of transition, $T_{\text{trs},i}$ the transition temperature of component i, T the absolute temperature, and R the universal gas constant.

Table 2. SLE Data for Three Binary Systems

system	x_1	T/K	x_1	T/K
TOA + 1-octanol	0.0000	257.85	0.6000	237.96
	0.0500	256.72	0.6999	232.33
	0.1000	255.46	0.7501	233.45
	0.2000	252.70	0.8001	234.68
	0.2998	249.85	0.9000	236.46
	0.4000	246.48	0.9498	237.82
	0.5001	242.15	1.0000	238.73
TOA + 1-decanol	0.0000	280.19	0.6999	261.48
	0.0504	279.27	0.7999	256.00
	0.1001	278.33	0.8995	246.82
	0.2002	276.69	0.9298	242.76
	0.3004	274.56	0.9500	238.15
	0.3999	272.14	0.9795	238.31
	0.4998	269.23	1.0000	238.73
	0.5997	265.71		
TOA + TBP	0.0000	194.31	0.4000	230.83
	0.0111	193.85	0.4963	232.31
	0.0300	206.30	0.6010	233.68
	0.0500	210.84	0.7000	234.26
	0.1001	218.65	0.7994	235.39
	0.2000	225.77	0.9008	236.50
	0.3000	228.62	1.0000	238.73

If a solid−solid phase transition does not occur in the considered temperature range, the last term can be neglected, and thereby the equation becomes

$$\ln(\gamma_i x_i) = -\frac{\Delta H_{\mathrm{fus},i}}{R}\left[\frac{1}{T} - \frac{1}{T_{\mathrm{fus},i}}\right] \qquad (3)$$

The results of the SLE measurements for the three binary systems are given in Table 2. The corresponding Figures 2 to 4 contain the experimental data and the correlation results using the NRTL and UNIQUAC equations. All of the binary systems, TOA + 1-octanol, TOA + 1-decanol, and TOA + TBP, showed single eutectic behaviors. The calculated G^E model parameters are given together in Table 3 with the root-mean-square deviations (rmsd's). The rmsd was calculated from eq 4.

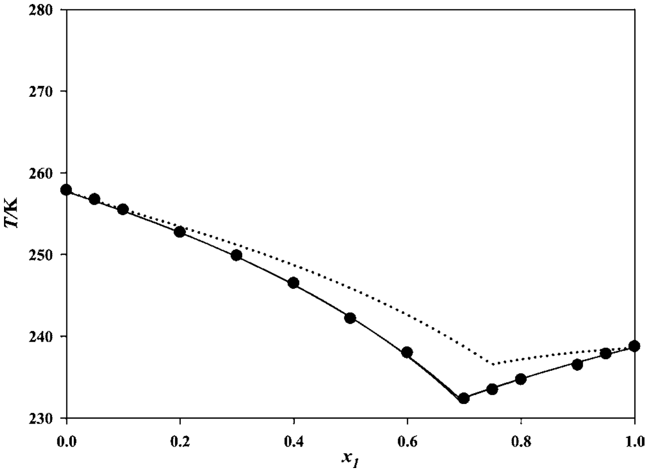

Figure 2. SLE for the system TOA (1) + 1-octanol (2). ●, experimental data; solid line, NRTL; dashed line, UNIQUAC; dotted line, modified UNIFAC (Dortmund).

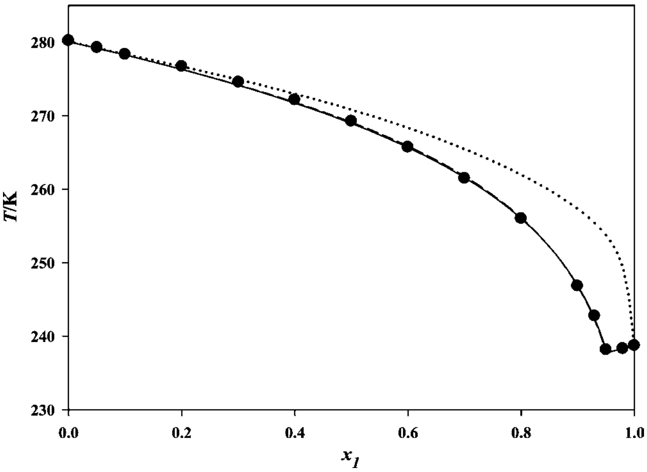

Figure 3. SLE for the system TOA (1) + 1-decanol (2). ●, experimental data; solid line, NRTL; dashed line, UNIQUAC; dotted line, modified UNIFAC (Dortmund).

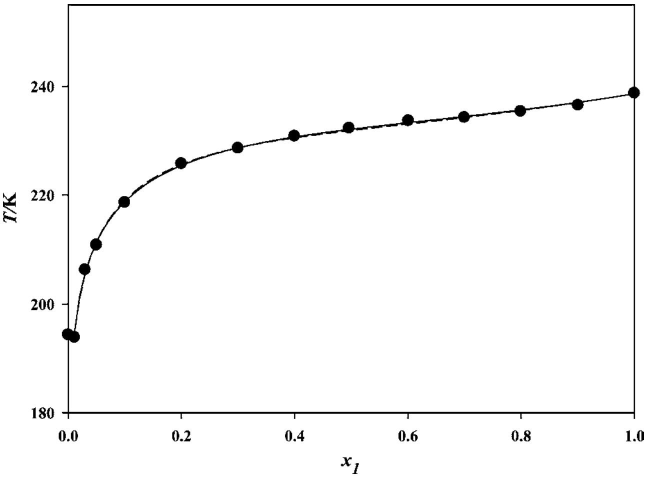

Figure 4. SLE for the system TOA (1) + TBP (2). ●, experimental data; solid line, NRTL; dashed line, UNIQUAC.

$$\mathrm{rmsd} = \sqrt{\frac{1}{n}\sum_{n}(T_{\exp} - T_{\mathrm{cal}})^2} \qquad (4)$$

The NRTL equation gives slightly better correlation results than the UNIQUAC equation. Their rmsd's from eq 4 were less than about 0.6 K. The interpolated eutectic points by the NRTL equation for the systems TOA + 1-octanol, TOA + 1-decanol, and TOA + TBP are $\{x_1 = 0.6900, 232.20\ \mathrm{K}\}$, $\{x_1 = 0.9515, 237.81\ \mathrm{K}\}$, and $\{x_1 = 0.0099, 193.95\ \mathrm{K}\}$, respectively.

However, predicted results of SLE by modified UNIFAC (Dortmund) were not reliable as shown in Figures 2 and 3. The calculated equilibrium temperatures by modified UNIFAC (Dortmund) showed higher values than the experimental data

Table 3. G^E Model Parameter and rmsd between the Calculated and the Experimental Data

model equation	system	A_{ij} / J·mol^{-1}	A_{ji} / J·mol^{-1}	α	rmsd
NRTL	TOA + 1-octanol	−2001.0482	2686.1698	0.3089	0.1990
	TOA + 1-decanol	1597.8236	−1050.4434	0.3063	0.2451
	TOA + TBP	1282.4629	1316.1190	0.2967	0.5916
UNIQUAC	TOA + 1-octanol	14.6441	92.8320		0.1997
	TOA + 1-decanol	944.3874	−684.7702		0.2653
	TOA + TBP	865.2135	−498.0006		0.6509

Table 4. Densities, Excess Molar Volumes, Refractive Indices, and Deviations in Molar Refractivity for the Measured Binary Systems at 298.15 K

system	x_1	ρ	V^E	n_D	ΔR
		$g \cdot cm^{-3}$	$cm^3 \cdot mol^{-1}$		$cm^3 \cdot mol^{-1}$
TOA + 1-octanol	0.0497	0.8208	−0.1625	1.4311	−7.6711
	0.1000	0.8197	−0.2996	1.4330	−13.6218
	0.2000	0.8178	−0.4977	1.4359	−21.1867
	0.3004	0.8160	−0.6126	1.4389	−24.5807
	0.4001	0.8145	−0.6646	1.4415	−25.1073
	0.4997	0.8131	−0.6745	1.4432	−23.6816
	0.6012	0.8119	−0.6543	1.4445	−20.7737
	0.7010	0.8107	−0.6052	1.4453	−16.7965
	0.8002	0.8097	−0.5111	1.4461	−11.9204
	0.8962	0.8087	−0.3410	1.4470	−6.4719
	0.9496	0.8081	−0.1916	1.4474	−3.1923
TOA + 1-decanol	0.0504	0.8254	−0.2258	1.4370	−5.1517
	0.0998	0.8240	−0.4072	1.4384	−9.1610
	0.2002	0.8216	−0.6706	1.4406	−14.6684
	0.3000	0.8193	−0.8266	1.4424	−17.4314
	0.4002	0.8173	−0.9152	1.4437	−18.2061
	0.5010	0.8154	−0.9641	1.4448	−17.4757
	0.6008	0.8138	−0.9843	1.4457	−15.5963
	0.7007	0.8123	−0.9631	1.4464	−12.7833
	0.8014	0.8107	−0.8542	1.4469	−9.1384
	0.9022	0.8092	−0.5705	1.4473	−4.7864
	0.9522	0.8086	−0.3252	1.4475	−2.4013
TOA + TBP	0.0499	0.9591	0.2213	1.4243	−1.6714
	0.0995	0.9465	0.4033	1.4259	−3.0957
	0.1998	0.9235	0.6783	1.4286	−5.2754
	0.3002	0.9030	0.8579	1.4315	−6.6025
	0.3997	0.8850	0.9581	1.4341	−7.1749
	0.5004	0.8686	0.9853	1.4366	−7.1124
	0.6001	0.8539	0.9360	1.4391	−6.5158
	0.7006	0.8406	0.8054	1.4413	−5.4611
	0.8008	0.8285	0.5953	1.4434	−4.0158
	0.9009	0.8175	0.3166	1.4454	−2.1975
	0.9514	0.8123	0.1580	1.4465	−1.1319
TBP + 1-octanol	0.0496	0.8337	0.1334	1.4270	−1.2461
	0.0998	0.8447	0.2575	1.4259	−2.3294
	0.1996	0.8650	0.4609	1.4243	−3.9698
	0.2995	0.8832	0.5965	1.4225	−4.9721
	0.4001	0.8997	0.6601	1.4216	−5.4027
	0.5002	0.9146	0.6548	1.4213	−5.3337
	0.5988	0.9281	0.5917	1.4213	−4.8595
	0.7011	0.9409	0.4787	1.4216	−4.0179
	0.8011	0.9525	0.3352	1.4219	−2.9112
	0.9008	0.9630	0.1724	1.4221	−1.5678
	0.9513	0.9680	0.0855	1.4224	−0.7990
TBP + 1-decanol	0.0496	0.8359	0.1329	1.4341	0.1329
	0.0999	0.8452	0.2714	1.4329	0.2714
	0.2008	0.8628	0.5227	1.4307	0.5227
	0.3001	0.8791	0.6998	1.4290	0.6998
	0.4004	0.8947	0.7900	1.4275	0.7900
	0.4996	0.9093	0.7949	1.4262	0.7949
	0.6007	0.9234	0.7294	1.4252	0.7294
	0.6981	0.9363	0.6167	1.4244	0.6167
	0.7985	0.9490	0.4624	1.4236	0.4624
	0.9003	0.9612	0.2635	1.4230	0.2635
	0.9505	0.9670	0.1422	1.4227	0.1422
1-octanol + 1-decanol	0.0500	0.8264	−0.0003	1.4350	−0.1060
	0.0996	0.8262	−0.0004	1.4346	−0.2034
	0.1996	0.8258	−0.0317	1.4340	−0.3716
	0.2997	0.8254	−0.0565	1.4333	−0.4964
	0.4005	0.8250	−0.0708	1.4325	−0.5762
	0.5006	0.8245	−0.0777	1.4318	−0.6104
	0.6005	0.8241	−0.0845	1.4310	−0.6004
	0.7006	0.8236	−0.0956	1.4301	−0.5444
	0.8002	0.8231	−0.1047	1.4293	−0.4365
	0.9000	0.8227	−0.0888	1.4284	−0.2631
	0.9507	0.8224	−0.0570	1.4279	−0.1427

as shown in the figures. In the case of the system TOA + TBP, the prediction was not carried out because exact modified UNIFAC parameters are not available for TBP.

Excess Molar Volumes and Molar Refractivity Deviations. The densities (ρ) and refractive indices (n_D) were measured at 298.15 K using a digital vibrating tube densimeter and a precision digital refractometer for pure components and the binary systems: TOA + 1-octanol, TOA + 1-decanol, TOA + TBP, TBP + 1-octanol, TBP + 1-decanol, and 1-octanol + 1-decanol. Then, the binary V^E and ΔR at 298.15 K were calculated and listed in Table 4 for the same systems.

In the case of V^E, the systems TOA + 1-octanol, TOA + 1-decanol, and 1-octanol + 1-decanol showed negative deviations because of the polarity of the alcohols and TOA. However, TBP contained mixtures that showed positive deviations from ideality. It may be caused by a longer carbon chain of 1-octanol and 1-decanol. They cannot easily enter the space among the three butyls of TBP. Also, the difference in shape and size of the molecules of the TBP and higher alcohols disturb the approach of each other. This makes them have positive excess volumes.

The value of ΔR for the same binary systems showed negative deviations from ideality except for the system TBP + 1-decanol. The refractive index of the mixture also strongly depends on the structure and molecular interactions of liquids. The

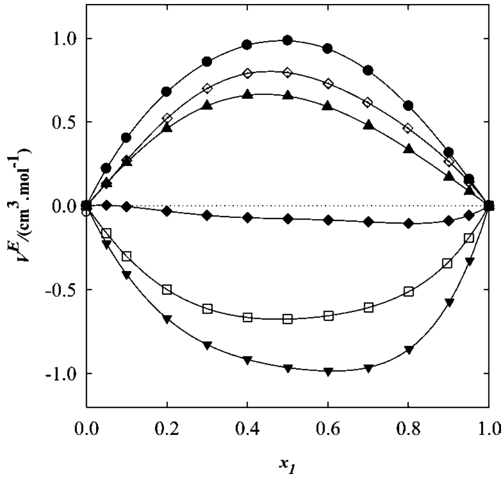

Figure 5. V^E ($cm^3 \cdot mol^{-1}$) for the binary systems at 298.15 K. □, TOA + 1-octanol; ▼, TOA + 1-decanol; ●, TOA + TBP; ▲, TBP + 1-octanol; ◇, TBP + 1-decanol; ◆, 1-octanol + 1-decanol. Solid curves were calculated from Redlich−Kister parameters.

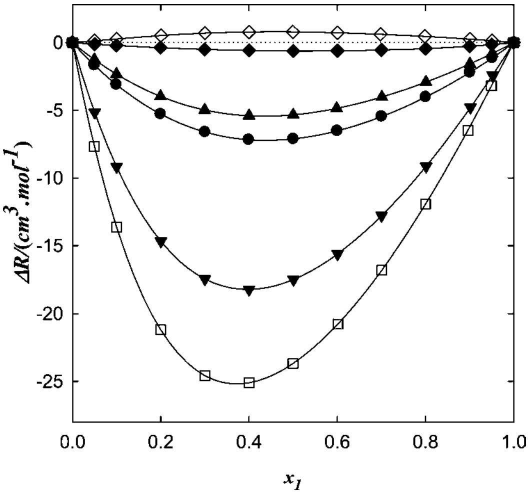

Figure 6. ΔR ($cm^3 \cdot mol^{-1}$) for the three binary systems at 298.15 K. □, TOA + 1-octanol; ▼, TOA + 1-decanol; ●, TOA + TBP; ▲, TBP + 1-octanol; ◇, TBP + 1-decanol; ◆, 1-octanol + 1-decanol. Solid curves were calculated from Redlich−Kister parameters.

Table 5. Fitted Redlich−Kister Parameters with the Standard Deviations for the Binary Systems at 298.15 K

	systems	A_1	A_2	A_3	A_4	σ_{st}
V^E	TOA + 1-octanol	−2.6978	0.1252	−1.2661	−0.5445	0.0066
	TOA + 1-decanol	−3.8550	−0.6893	−2.5453	−0.7855	0.0090
	TOA + TBP	3.9414	−0.2073	0.1284	−0.6039	0.0090
	TBP + 1-octanol	2.6195	−0.7330	−0.3452	0.2321	0.0099
	TBP + 1-decanol	3.1789	−0.6615	−0.3170	0.9524	0.0071
	1-octanol + 1-decanol	−0.3106	−0.1137	−0.3225	−0.7385	0.0080
ΔR	TOA + 1-octanol	−94.6972	44.2655	−24.4625	10.9252	0.0098
	TOA + 1-decanol	−69.9539	26.7925	−12.7455	4.6316	0.0098
	TOA + TBP	−28.4549	6.9139	−1.7546	−1.1210	0.0099
	TBP + 1-octanol	−9.1086	1.6385	−0.4909	0.1795	0.0040
	TBP + 1-decanol	−0.6210	10.5667	13.9840	5.3391	0.0097
	1-octanol + 1-decanol	−2.4414	−0.2459	−0.2408	−0.2532	0.0040

dipole−dipole interactions are weak in higher 1-alkanols owing to the decrease in their polarizability with increasing chain length. However, the chain length increases the change in the refractive index which becomes more negative.[19] These complex concepts make ΔR negative for the systems TOA + TBP and TBP + 1-octanol. The binary V^E and ΔR data were correlated well with the Redlich−Kister equation of the following form.

$$V^E \text{ or } \Delta R/\text{cm}^3\cdot\text{mol}^{-1} = x_1x_2\sum_{i=1}^{n}A_i(x_1-x_2)^{i-1} \qquad (5)$$

Table 5 shows the correlated Redlich−Kister parameters with the standard deviation for each binary system. Figures 5 and 6 illustrate the measured binary V^E and ΔR with correlation results, respectively. The solid lines are calculated from the correlated Redlich−Kister parameters. In addition, the ternary V^E and ΔR for the systems TOA + TBP + 1-octanol, TOA + 1-octanol + 1-decanol, TOA + TBP + 1-decanol, and TBP + 1-octanol + 1-decanol were calculated by Radojkovič equation using the binary correlated parameters in Table 5. Figures 7 and 8 show these calculated isoclines of ternary V^E and ΔR data. They have

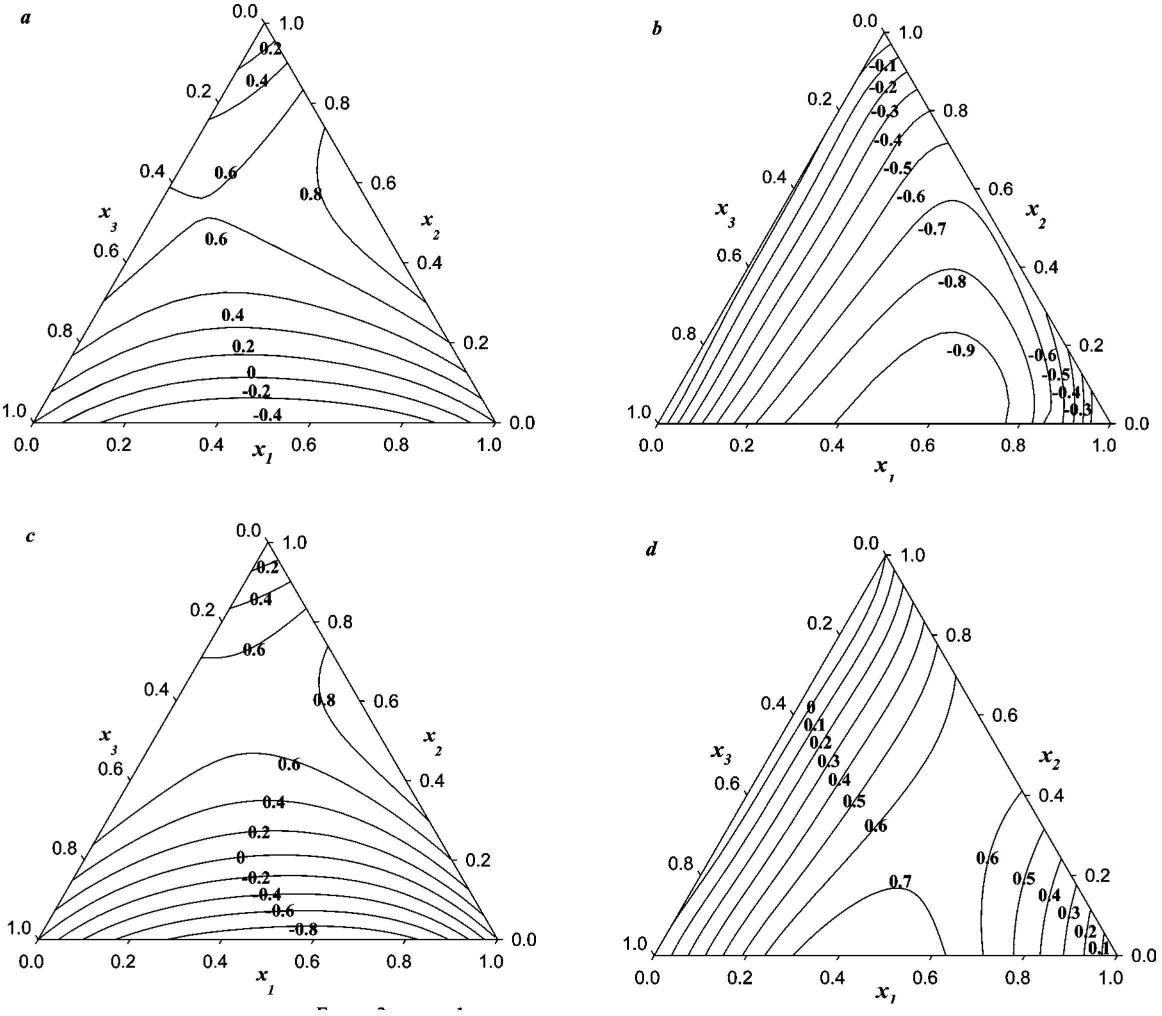

Figure 7. Isoclines of V^E (cm^3·mol^{-1}) for ternary systems at 298.15 K. (a) TOA + TBP + 1-octanol; (b) TOA + 1-octanol + 1-decanol; (c) TOA + TBP + 1-decanol; (d) TBP + 1-octanol + 1-decanol.

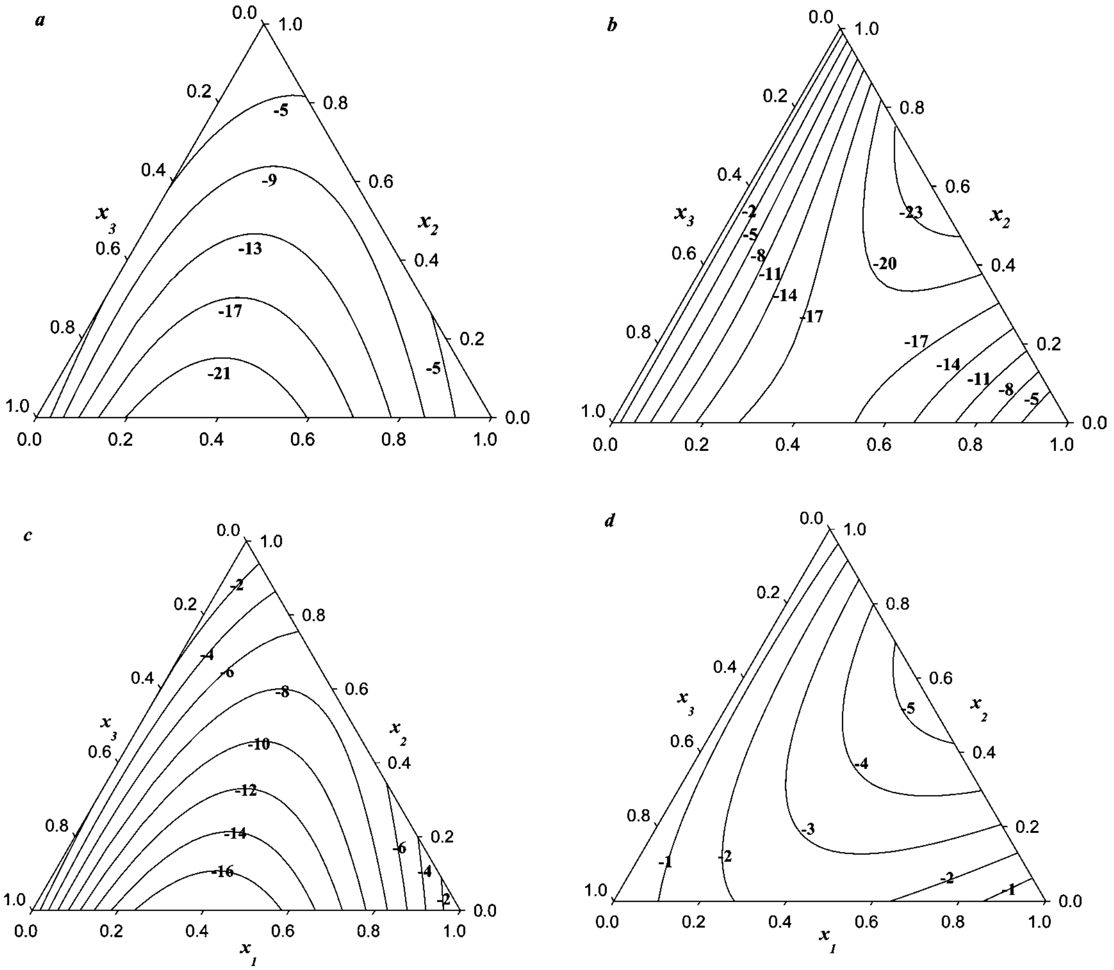

Figure 8. Isoclines of ΔR ($\text{cm}^3 \cdot \text{mol}^{-1}$) for the ternary systems at 298.15 K. (a) TOA + TBP + 1-octanol; (b) TOA + 1-octanol + 1-decanol; (c) TOA + TBP + 1-decanol; (d) TBP + 1-octanol + 1-decanol.

positive and negative values according to the concentration and combination of solvents as we make an estimate from their binary V^E and ΔR data.

Conclusion

The solid−liquid equilibria for the binary systems of extractive solvent and modifiers for molybdenum were measured at the temperature range of (194 to 281) K by the visual method. The systems TOA + 1-octanol, TOA + 1-decanol, and TOA + TBP have a single eutectic point. The binary SLE data were correlated well with the NRTL and UNIQUAC equations. However, the prediction results of SLE by the modified UNIFAC equation are not reliable for these systems. The excess molar volumes (V^E) and molar refractivity deviations (ΔR) were determined for the following systems: TOA + 1-octanol, TOA + 1-decanol, TOA + TBP, TBP + 1-octanol, TBP + 1-decanol, and 1-octanol + 1-decanol. The V^E and ΔR data of the experiment for the above binary systems were correlated well with the Redlich−Kister equation. The correlated binary parameters are applied reliably to calculate ternary V^E and ΔR data.

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