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Liquid–Liquid Equilibria for Three Ternary and Six Quaternary Systems Containing Sulfolane, *n*-Heptane, Toluene, 2-Propanol, and Water at 303.15 K

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Liquid–liquid phase equilibrium data have been measured for the ternary systems *n*-heptane–toluene–sulfolane, toluene–sulfolane–water, and *n*-heptane–2-propanol–sulfolane at 303.15 K by gas-chromatoraphic analysis of the tie-line material. Limited data have also been obtained for six quaternary systems. Four of these are for *n*-heptane–toluene–sulfolane–water with water/sulfolane content ranging from 2 to 10 mass %, and two are for *n*-heptane–toluene–sulfolane–2-propanol with 2-propanol/sulfolane content of 10 and 20 mass %.

Sulfolane is widely used as a solvent for the extraction of aromatic hydrocarbons from refinery process streams, but published quantitative phase equilibrium data are scarce. In an earlier paper (*1*) we reported vapor–liquid equilibria for several binary sulfolane-containing systems as part of a project to investigate vapor–liquid and liquid–liquid phase relationships of the type encountered in liquid extraction processes. This paper is concerned with liquid–liquid equilibria for the ternary systems *n*-heptane–toluene–sulfolane, toluene–sulfolane–water, and *n*-heptane–2-propanol–sulfolane at 303.15 K. The results of studies on the effect of the addition of small quantities of water and 2-propanol as solvent modifiers upon the system *n*-heptane–toluene–sulfolane at 303.15 K are also reported here. These were carried out to ascertain the variation of both the solvent selectivity and the hydrocarbon solubility with various quantities of solvent modifier. In the present case, water acts as an antisolvent, increasing the size of the two-phase envelope. Conversely, 2-propanol decreases the size of the two-phase envelope and may be described as a prosolvent.

Experimental Section

Materials. Toluene and 2-propanol were BDH high-purity "Aristar" grade reagents. These were dried with activated type 5A molecular sieves but otherwise used as supplied. The toluene was certified by the manufacturers to be of a minimum purity of 99.95 mass % and the 2-propanol to have a maximum water content of 0.1 mass %, with all other impurities to be below 0.001 mass %. This water content was reduced to below 0.01 mass %, as confirmed by gas chromatography.

The *n*-heptane was laboratory reagent grade obtained from Fisons Ltd. This was passed through a silica gel column (to remove aromatics) and then distilled at atmospheric pressure (25-plate, 25-mm i.d. Oldershaw column, 5:1 reflux ratio). The *n*-heptane boiling over 0.1 K was collected and stored over molecular sieves.

Anhydrous sulfolane supplied by the Shell Chemical Co. was dried with molecular sieves and then twice vacuum distilled from phosphorous pentoxide at a pressure below 1 mmHg to yield a colorless, odorless product. To minimize the contact of this deliquescent reagent with moist air, we kept the product in stoppered bottles in a desiccator.

Water was freshly distilled before use. Physical properties of these materials were listed in an earlier paper (*1*).

Equilibrium Measurements. The liquid–liquid equilibrium measurements were made by using a 250-cm^3 cylindrical glass vessel of U-shaped cross section. The top was closed, using a PTFE gasket, by a 6-mm thick stainless-steel plate carrying a stainless-steel stirrer, a thermistor pocket, a closable sampling point, and a tube for the entry of dry nitrogen. The whole was immersed in a water thermostat controlled at 303.15 ± 0.05 K. A thermistor (ITT type F23D) was used to measure temperature in conjunction with an automatic digital bridge (Solartron type EX1732). The thermistor was calibrated against a short-range (5 K) precision mercury thermometer (IPTS 68) certified by the National Physical Laboratory.

The cell was purged with dry nitrogen before being charged. The mixture was stirred for at least 2 h and then allowed to settle. Samples (5 cm^3) of the two phases were withdrawn for analysis by glass syringes equipped with stainless-steel hypodermic needles and then stored in sealed glass containers at a temperature of 303.65 ± 0.5 K in an air bath to await analysis. Sampling techniques, designed to eliminate the possibility of contamination, are given in detail by Clayton (*2*).

Analysis. A Pye-Unicam Series 104 gas chromatograph, equipped with a thermal conductivity detector, was used in conjunction with a Honeywell linear amplifier and integrator. The glass columns were 0.9 m × 3 m i.d., charged with 10 mass % Apiezon L on Chromosorb W, and the carrier gas was helium. For some of the water-containing samples a packing of Porapak Q was used. The calibration and calculation procedure followed that given by Smith and Bowden (*3*). The precision of the measurements was considered to be ±0.003 in mass fraction for the ternary systems and ±0.001 in mass fraction for the *n*-heptane–sulfolane binary system. The accuracy in the quaternary systems was considered to be inferior to that for the ternary systems, owing to the difficulty of obtaining complete resolution of the sulfolane/modifier peaks.

Results and Discussion

Ternary Systems. Tie-line data for the three systems are reported in Tables I–III, as both mass and mole fractions. The mutual solubilities of the partially miscible binary systems *n*-

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Table I. Liquid-Liquid Equilibria for *n*-Heptane (1)-Toluene (2)-Sulfolane (3) at 303.15 K and Tie-Line Data for Raffinate (*n*-Heptane-Rich) and Extract (Sulfolane-Rich) Phases

	mass fractions			mole fractions		
phase	1	2	3	1	2	3
raff	0.188	0.592	0.220	0.185	0.634	0.181
ext	0.088	0.460	0.452	0.091	0.518	0.391
raff	0.296	0.594	0.110	0.286	0.625	0.089
ext	0.039	0.343	0.618	0.042	0.402	0.556
raff	0.347	0.572	0.081	0.335	0.600	0.065
ext	0.031	0.286	0.683	0.034	0.341	0.625
raff	0.357	0.569	0.074	0.344	0.597	0.059
ext	0.030	0.282	0.688	0.034	0.336	0.630
raff	0.397	0.548	0.055	0.382	0.574	0.044
ext	0.027	0.265	0.708	0.029	0.319	0.652
raff	0.573	0.403	0.024	0.556	0.424	0.020
ext	0.015	0.157	0.828	0.017	0.195	0.788
raff	0.591	0.383	0.026	0.574	0.405	0.021
ext	0.016	0.146	0.838	0.018	0.182	0.800
raff	0.615	0.365	0.020	0.597	0.386	0.017
ext	0.015	0.144	0.841	0.017	0.180	0.803
raff	0.652	0.334	0.014	0.635	0.353	0.012
ext	0.014	0.124	0.862	0.016	0.155	0.829
raff	0.677	0.304	0.019	0.662	0.323	0.015
ext	0.012	0.110	0.878	0.015	0.138	0.847
raff	0.753	0.234	0.013	0.739	0.251	0.010
ext	0.011	0.085	0.904	0.013	0.107	0.880
raff	0.920	0.075	0.005	0.915	0.081	0.004
ext	0.008	0.025	0.967	0.010	0.032	0.958
raff	0.996	0.0	0.004	0.996	0.0	0.004
ext	0.009	0.0	0.991	0.011	0.0	0.989
plait point[a]	0.109	0.523	0.368	0.110	0.578	0.312

[a] Calculated.

Table II. Liquid-Liquid Equilibria for Toluene (1)-Sulfolane (2)-Water (3) at 303.15 K and Tie-Line Data for Raffinate (Toluene-Rich) and Extract (Water-Rich) Phases

	mass fractions			mole fractions		
phase	1	2	3	1	2	3
raff	0.443	0.532	0.025	0.454	0.416	0.130
ext	0.084	0.737	0.179	0.054	0.362	0.584
raff	0.574	0.414	0.012	0.603	0.334	0.063
ext	0.045	0.707	0.248	0.025	0.293	0.682
raff	0.619	0.372	0.009	0.651	0.300	0.049
ext	0.033	0.677	0.290	0.016	0.255	0.729
raff	0.689	0.307	0.004	0.729	0.249	0.022
ext	0.023	0.631	0.346	0.010	0.213	0.777
raff	0.723	0.273	0.004	0.760	0.221	0.019
ext	0.014	0.593	0.393	0.006	0.183	0.811
raff	0.815	0.183	0.002	0.845	0.145	0.010
ext	0.005	0.529	0.466	0.002	0.145	0.853
raff	0.858	0.141	0.001	0.883	0.111	0.006
ext	0.004	0.469	0.527	0.001	0.118	0.881
raff[a]	0.9994	0.0	0.0006	0.9970	0.0	0.0030
ext[a]	0.0005	0.0	0.9995	0.0001	0.0	0.9999
plait point[b]	0.255	0.677	0.068	0.228	0.464	0.308

[a] Mutual solubility data from ref *4*. [b] Calculated.

heptane-sulfolane and toluene-water are also given in the tables, the latter values being the data of Polak and Lu (*4*) extrapolated to 303.15 K. The values reported here for the *n*-heptane-sulfolane system agree to within 0.001 mass fraction with those of Advei et al. (*5*). The coordinates of the plait points given in the tables were calculated by the method of Treybal et al. (*6*).

The ternary systems are shown as triangular diagrams in Figures 1-3. The only literature data available for comparison are for the *n*-heptane-toluene-sulfolane system, but at different temperatures than those used here. De Fre and Verhoeye (*7*) examined the system at 298.15, 323.15, and 373.15 K. The results presented here are in excellent agreement with regard both to the size of the solubility envelope and to the slope of the tie lines. Tripathi et al. (*8*) studied the system at 298.15,

Table III. Liquid-Liquid Equilibria for *n*-Heptane (1)-2-Propanol (2)-Sulfolane (3) at 303.15 K and Tie-Line Data for Raffinate (*n*-Heptane-Rich) and Extract (Sulfolane-Rich) Phases

	mass fractions			mole fractions		
phase	1	2	3	1	2	3
raff	0.360	0.434	0.206	0.287	0.576	0.137
ext	0.051	0.255	0.694	0.049	0.402	0.549
raff	0.452	0.428	0.120	0.357	0.564	0.079
ext	0.046	0.244	0.710	0.044	0.390	0.566
raff	0.487	0.405	0.108	0.388	0.540	0.072
ext	0.034	0.221	0.745	0.033	0.361	0.606
raff	0.659	0.289	0.052	0.556	0.407	0.037
ext	0.030	0.189	0.781	0.030	0.316	0.654
raff	0.723	0.234	0.043	0.629	0.339	0.032
ext	0.035	0.163	0.802	0.036	0.278	0.686
raff	0.828	0.159	0.013	0.749	0.241	0.010
ext	0.026	0.148	0.826	0.027	0.257	0.716
raff	0.895	0.095	0.010	0.843	0.149	0.008
ext	0.019	0.123	0.858	0.020	0.218	0.762
raff	0.958	0.037	0.005	0.936	0.060	0.004
ext	0.014	0.080	0.906	0.015	0.147	0.838
raff	0.982	0.014	0.004	0.980	0.010	0.010
ext	0.010	0.028	0.962	0.012	0.054	0.934
raff	0.993	0.003	0.004	0.992	0.005	0.003
ext	0.009	0.017	0.974	0.011	0.033	0.956
raff	0.996	0.0	0.004	0.996	0.0	0.004
ext	0.009	0.0	0.991	0.011	0.0	0.989
plait point[a]	0.091	0.337	0.572	0.081	0.497	0.422

[a] Calculated.

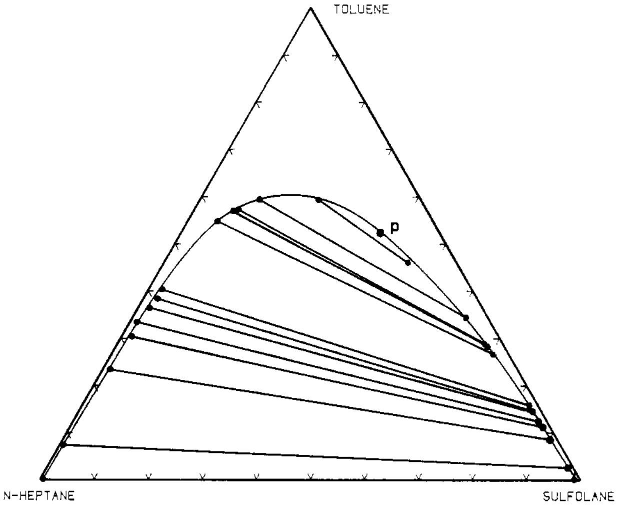

Figure 1. Phase equilibria for *n*-heptane-toluene-sulfolane at 303.15 K (mass fractions).

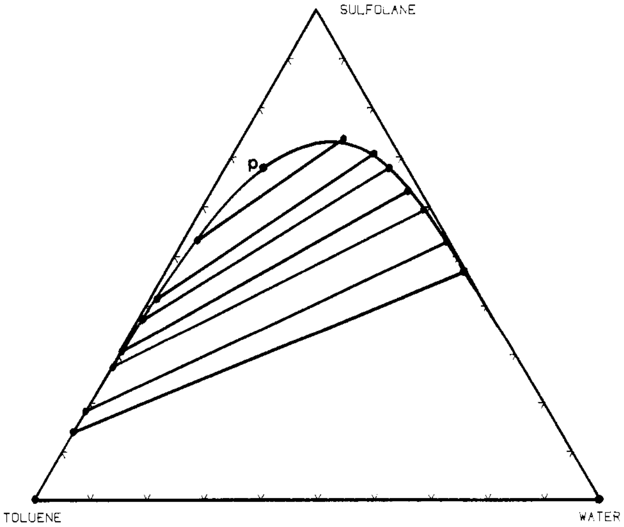

Figure 2. Phase equilibria for toluene-sulfolane-water at 303.15 K (mass fractions).

Table IV. Liquid-Liquid Equilibria for *n*-Heptane (1)-Toluene (2)-Sulfolane + Water (3) at 303.15 K and Tie-Line Data (Mass Fractions) for Raffinate (*n*-Heptane-Rich) and Extract (Sulfolane-Rich) Phases

	2% water in solvent			4% water in solvent			7% water in solvent			10% water in solvent		
phase	1	2	3	1	2	3	1	2	3	1	2	3
raff	0.143	0.633	0.224	0.114	0.655	0.231	0.058	0.689	0.253	0.164	0.737	0.099
ext	0.047	0.436	0.517	0.024	0.377	0.599	0.009	0.286	0.705	0.003	0.142	0.855
raff	0.201	0.645	0.154	0.199	0.687	0.114	0.201	0.698	0.101	0.390	0.576	0.034
ext	0.034	0.366	0.600	0.016	0.264	0.720	0.008	0.210	0.782	0.003	0.108	0.889
raff	0.352	0.597	0.051	0.303	0.640	0.057	0.280	0.651	0.069	0.502	0.480	0.018
ext	0.020	0.269	0.711	0.011	0.215	0.774	0.004	0.157	0.839	0.001	0.075	0.924
raff	0.518	0.458	0.024	0.410	0.550	0.040	0.417	0.556	0.027	0.628	0.364	0.008
ext	0.010	0.159	0.831	0.010	0.181	0.809	0.004	0.129	0.867	0.002	0.052	0.946
raff	0.553	0.427	0.020	0.528	0.455	0.017	0.556	0.432	0.012	0.808	0.191	0.001
ext	0.009	0.145	0.846	0.006	0.145	0.849	0.003	0.093	0.904	0.001	0.026	0.973
raff	0.730	0.261	0.009	0.805	0.193	0.002	0.703	0.290	0.007	0.922	0.072	0.006
ext	0.009	0.094	0.897	0.005	0.054	0.941	0.003	0.053	0.944	0.001	0.011	0.988
raff	0.934	0.064	0.002	0.959	0.040	0.001	0.763	0.228	0.009			
ext	0.004	0.020	0.976	0.003	0.011	0.986	0.002	0.041	0.957			

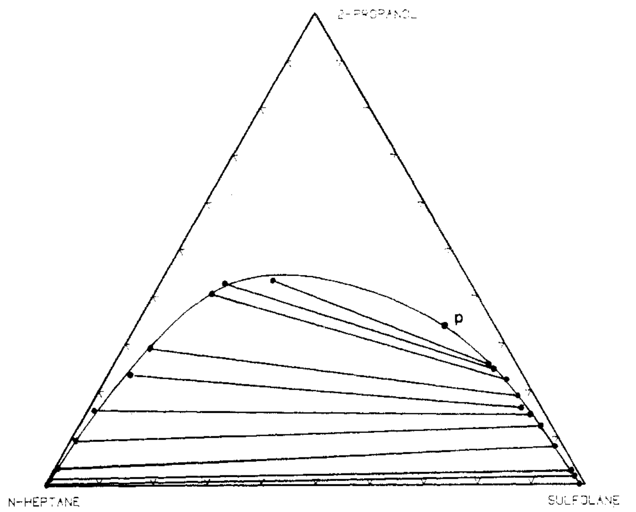

Figure 3. Phase equilibria for *n*-heptane-2-propanol-sulfolane at 303.15 K (mass fractions).

313.15, and 323.15 K, but here the agreement is slightly less good in the vicinity of the plait point. The tie-line slopes show small deviations from both the present results and those of De Fre and Verhoeye. A comparison of the three different sets of data is given in Figure 4, in which solvent selectivity is shown as a function of solvent-free mass fraction of toluene in the raffinate phase. Selectivity, β, is defined here in terms of mass fraction as

$$\beta = \frac{x(\text{toluene,extract})/x(\text{toluene,raffinate})}{x(n\text{-heptane,extract})/x(n\text{-heptane,raffinate})}$$

It is interesting to note that the system *n*-heptane-2-propanol-sulfolane exhibits solutropic behavior. This type of system exhibits a marked change in tie-line slope from positive to negative within the two-phase envelope.

The prediction of liquid-liquid equilibria has also been investigated by using activity coefficients for the constituent binary systems expressed in the form of the nonrandom two-liquid (NRTL) equation. The constants were previously determined from vapor-liquid equilibria (*1*). It seems inappropriate to discuss these results in detail in view of a recent comprehensive report by De Fre and Verhoeye (*9*) on such predictions in sulfolane systems. The method used here and the results are fully documented by Clayton (*2*). Observations broadly similar to those of De Fre and Verhoeye can be drawn, in that the predicted heterogeneous area tends to be larger than that determined experimentally. This effect is mainly noticeable near the plait point. In the region of heterogeneity remote from the plait point the slope of the tie lines and the two phase boundaries are satisfactorily described by the NRTL equation using constants derived from binary data.

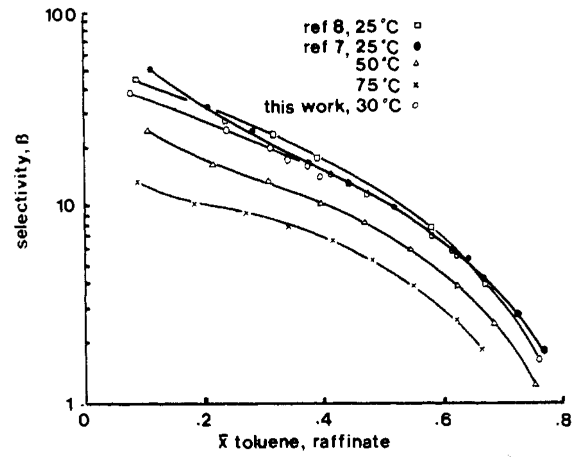

Figure 4. Solvent selectivity at different temperatures.

Table V. Liquid-Liquid Equilibria for *n*-Heptane (1)-Toluene (2)-Sulfolane + 2-Propanol (3) at 303.15 K and Tie-Line Data (Weight Fractions) for Raffinate (*n*-Heptane-Rich) and Extract (Sulfolane-Rich) Phases

	10% 2-propanol in solvent			20% 2-propanol in solvent		
phase	1	2	3	1	2	3
raff	0.330	0.517	0.153	0.335	0.496	0.169
ext	0.065	0.341	0.594	0.071	0.337	0.592
raff	0.392	0.509	0.099	0.498	0.393	0.109
ext	0.045	0.294	0.661	0.044	0.226	0.730
raff	0.548	0.400	0.052	0.575	0.336	0.089
ext	0.022	0.200	0.778	0.035	0.177	0.788
raff	0.608	0.348	0.044	0.692	0.237	0.071
ext	0.020	0.158	0.822	0.030	0.109	0.861
raff	0.731	0.239	0.030	0.697	0.231	0.072
ext	0.019	0.100	0.881	0.028	0.109	0.863
raff	0.845	0.128	0.027	0.806	0.128	0.066
ext	0.013	0.054	0.933	0.020	0.063	0.917
raff				0.884	0.021	0.095
ext				0.016	0.007	0.977

Quaternary Systems. The gas-chromatographic analysis of the small quantities of solvent modifier presented some difficulty owing to the very small peak size, comparable in some cases to the limit of detection of the equipment, and to incomplete resolution from the solvent peak. Consequently, the quaternary data reported in Tables IV and V give the total of the mass fractions of solvent and modifier as a pseudocomponent.

A difficulty arises in the rigorous representation of quaternary liquid-liquid data since triangular coordinates no longer suffice. In this paper the data are presented in Figure 5 as solvent selectivity, β, against solvent-free mass fraction of toluene in

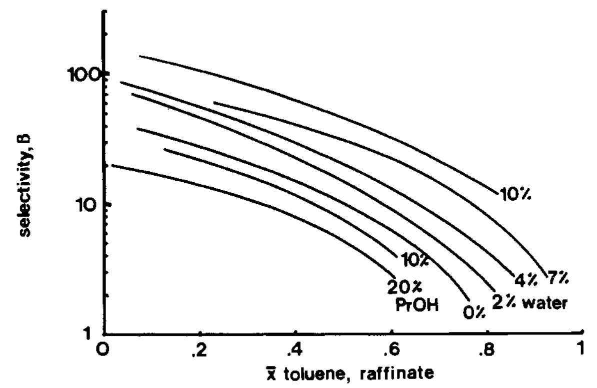

Figure 5. Effect of solvent modifiers on selectivity.

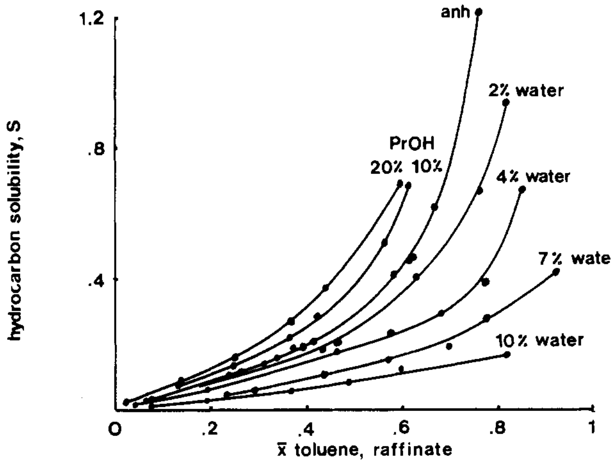

Figure 6. Effect of solvent modifiers on hydrocarbon solubility in the extract phase.

the raffinate, $\bar{x}$. The data have been smoothed in this plot by least-squares fitting to a quadratic line. Figure 6 shows the total hydrocarbon solubility, S, in the extract solvent, $[x(n\text{-heptane}) + x(\text{toluene})]/x(\text{solvent})$, plotted against the solvent-free mass fraction of toluene in the raffinate, $\bar{x}$. It is apparent that increasing the water content in the modified solvent increases the selectivity and reduces the hydrocarbon solubility, while increasing the 2-propanol content reduces selectivity and increases the hydrocarbon solubility. On a mass basis water is a considerably more effective antisolvent than 2-propanol is a prosolvent.

In multistage, countercurrent extraction, using sulfolane, of toluene from a heptane–toluene mixture the extract purity can evidently be increased to any desired level by using a water-modified solvent. This is achieved at the expense of some increase in the solvent throughput owing to the reduced hydrocarbon solubility in the extract solvent. A comparison of the effect of the solvent modifiers on the selectivities with the effect of temperature changes in the *n*-heptane–toluene–sulfolane system may be made by examination of Figures 4 and 5. Here it can clearly be seen that the addition of small amounts (approximately 2% by mass) of water to sulfolane has a more pronounced effect on the solvent selectivity than a decrease in temperature of 25 K.

Glossary

x	liquid-phase mass fraction
β	solvent selectivity = $[x(\text{toluene,extract})/x(\text{toluene, raffinate})]/[x(n\text{-heptane,extract})/x(n\text{-heptane, raffinate})]$
S	hydrocarbon solubility in extract = $[x(n\text{-heptane, extract}) + x(\text{toluene,extract})]/x(\text{solvent,extract})$
$\bar{x}$	solvent-free mass fraction

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Viscosity of KNO_3–$NaNO_2$–$NaNO_3$ Mixtures

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The viscosities of two molten mixtures of KNO_3–$NaNO_2$–$NaNO_3$ have been measured. Mixture 1 was the eutectic of composition 53/40/7 wt %; the composition of mixture 2 simulated the thermal decomposition of the previous eutectic and was 52/33.6/14.4 wt %. The results can be expressed by $\eta_1(\text{mPa s}) = 0.5631 \exp[-146.9794T^{-1} + (57.4265 \times 10^4)T^{-2}]$ and $\eta_2(\text{mPa s}) = 0.8392 \exp[-498.6183T^{-1} + (68.4889 \times 10^4)T^{-2}]$, respectively.

The eutectic mixture of KNO_3–$NaNO_2$–$NaNO_3$ is known as a heat-transfer medium with many proven advantages. It is safe, nontoxic, noncorrosive, and low-cost, operates at atmospheric pressure, and has exceptional heat-transfer characteristics, thermal stability, and a wide liquid temperature range. In connection with a thermal heat-storage program, the present work was initiated to obtain viscosity data for this molten eutectic and also for a quite similar mixture.

The eutectic KNO_3–$NaNO_2$–$NaNO_3$ mixture (53/40/7 wt % was supplied by Electricité de France, Direction des Etudes et Recherches. The second mixture had the composition 52/33.6/14.4 wt % and was synthetized from Prolabo R.P. Normapur chemicals; this composition was chosen to simulate that of the thermal decomposition of the previous eutectic. In the following, these mixtures will be quoted as mixture 1 and mixture 2, respectively. All salts and mixtures were dried under vacuum for several days at 120 °C.

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