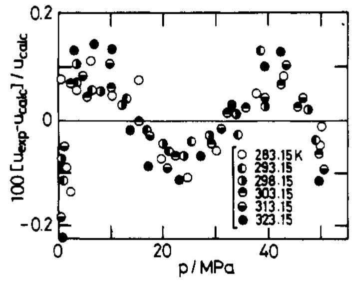

Figure 4. Deviation plot for ultrasonic speed *u*.

ultrasonic speeds are strongly dependent upon pressure close to the saturated vapor pressure especially at high temperature. This tendency is similar to that of other thermodynamic properties, i.e., the *pVT* relation (*2*) and isobaric heat capacity (*4*).

From the coefficients for eq 2, the speed in the liquid phase u_{p_s} at the vapor pressure p_s was calculated, and the results are also shown in Table II with the p_s derived from the equation reported in ref *14*. Sakiades and Costes (*15*) estimated the additivity coefficient *B* from molecular structural considerations using the experimental *u* values, and calculated the value of speed *u* by Rao's equation (*16*) [$u = (B\rho/M)^3$, where ρ = density, *M* = molecular weight]. It is well-known that this method can be adapted conveniently to some organic liquids at atmospheric pressure. Kokernak and Feldman (*12*) measured the ultrasonic speed in the liquid phase of dichlorodifluoromethane (R12), and calculated the *B* value for the fluorine atom. From this value and the *B* values of other atoms estimated by Sakiades and Costes, the speeds in some liquids including fluorinated hydrocarbons were estimated. According to their report, the *u* value in the liquid phase of dichlorotetrafluoroethane (R114) at 298.15 K was 478.5 m·s^{-1}. However, this value is lower by about 15% than that obtained by eq 2 in this work. The vapor pressures are 0.6516 MPa for R12 (*17*) and 0.2144 MPa for R114 (*14*) at 298.15 K. In ref *12*, the ultrasonic speed in R114 was obtained by using the additivity coefficients of fluorine atom taken from the *u* value in R12, which has a different vapor pressure from that for R114. Thus, a large discrepancy in ultrasonic speed would be expected between these two refrigerants. It may be presumed that application of this theoretical method to predict the ultrasonic speed in refrigerants is unreasonable. Consequently, direct measurements of ultrasonic speed in the liquid phase of individual refrigerants are expected to continue in the future.

Registry No. R114, 76-14-2.

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Viscosities, Densities, and Activation Energies of Viscous Flow of the Ternary Systems *n*-Hexane–Benzyl Alcohol–Toluene, *n*-Hexane–Benzyl Alcohol–Chlorobenzene, and *n*-Hexane–Benzyl Alcohol–1-Hexanol and Their Partially Miscible Binary Subsystem *n*-Hexane–Benzyl Alcohol at 30, 40, 50, and 60 °C

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Mixture viscosities and densities of the partially miscible ternary systems of toluene, chlorobenzene, and 1-hexanol with their partially miscible binary subsystem *n*-hexane–benzyl alcohol were measured at 30, 40, 50, and 60 °C. Activation enthalpies and entropies for viscous flow have been obtained and their variations with composition have been discussed.

Introduction

Viscosities and activation energies of viscous flow of several binary as well as ternary mixtures, reported by us earlier (*1–5*), dealt with systems which are completely miscible in the temperature range studied. Herein are results of our similar investigation of the partially miscible ternary systems *n*-hexane (1)–benzyl alcohol (2)–toluene (3), *n*-hexane, (1)–benzyl alcohol (2)–chlorobenzene (3), and *n*-hexane (1)–benzyl alcohol (2)–1-hexanol (3) and their partially miscible binary subsystem *n*-hexane (1)–benzyl alcohol (2) at 30, 40, 50, and 60 °C.

Experimental Section

Materials. Liquids used were the same as in the previous studies (*1–5*). However, their purity, after fractional distillation

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Table I. Comparison of the Experimental and Literature Values of the Densities, Viscosities, and Refractive Indices for the Ternary Components Used

parameter	t, °C	n-hexane	toluene	chlorobenzene	1-hexanol	benzyl alcohol
ρ, g mL^{-1}	25	0.6549	0.8623	1.1011	0.8160	1.0413
		(0.65481)^a	(0.86231)^a	(1.1011)^b	(0.81590)^a	(1.04127)^a
η, cP	25	0.299	0.552	0.758	4.59	4.648^d
		(0.2985)^a	(0.5516)^a	(0.7580)^b	(4.5920)^a	(4.650)^a
n_D	25	1.37225	1.49415	1.52165	1.41610	1.53840
		(1.37226)^a	(1.49413)^a	(1.52160)^c	(1.41610)^a	(1.53837)^a
M		86.178^a	92.142^a	112.56^a	102.178^a	108.141^a

[a] Reference 11. [b] Reference 12. [c] Reference 13. [d] At 30 °C.

Table II. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m{}^*$ and Entropy of Activation $\Delta S_m{}^*$ for Data Points in the Miscible Region of the Ternary System *n*-Hexane (1)–Benzyl Alcohol (2)–Toluene (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m{}^*$, cal mol^{-1}	$\Delta S_m{}^*$, cal mol^{-1} K^{-1}
0.0487	0.3508	30	0.9121	0.9421	3576.6	+0.813
		40	0.9075	0.8064	2940.8	−1.30
		50	0.9018	0.6759	2384.4	−2.97
		60	0.8970	0.5894	1828.0	−4.60
0.1151	0.4183	30	0.9085	1.017	4132.9	+2.48
		40	0.9038	0.8606	3497.1	+0.33
		50	0.8969	0.7207	2781.8	−1.89
		60	0.8929	0.6307	2145.9	−3.81
0.1671	0.2763	30	0.8703	0.7243	3020.3	−0.554
		40	0.8659	0.6281	2861.3	−1.11
		50	0.8584	0.5432	2781.8	−1.37
		60	0.8525	0.4849	2622.9	−1.89
0.2179	0.5754	30	0.9129	1.337	4530.4	+3.21
		40	0.9082	1.095	4132.9	+1.86
		50	0.9023	0.9064	3656.1	+0.332
		60	0.8996	0.7729	3179.2	−1.13
0.2889	0.6482	30	0.9085	1.502	4609.9	+3.22
		40	0.9036	1.239	4132.9	+1.58
		50	0.9009	0.9970	3735.6	+0.371
		60	0.8976	0.8451	3338.2	−0.849
0.3455	0.5053	30	0.8704	1.046	3338.3	−0.289
		40	0.8648	0.8841	3099.7	−1.08
		50	0.8574	0.7323	2781.8	−2.02
		60	0.8528	0.6504	2543.4	−2.77
0.4065	0.1574	30	0.7927	0.4985	3020.3	+0.073
		40	0.7885	0.4475	2702.3	−1.06
		50	0.7845	0.3926	2384.4	−2.06
		60	0.7810	0.3497	1987.0	−3.25
0.4843	0.2280	30	0.7921	0.5404	2622.9	−1.42
		40	0.7873	0.4833	2463.9	−1.99
		50	0.7799	0.4165	2145.9	−2.94
		60	0.7760	0.3749	1987.0	−3.42
0.5476	0.0696	30	0.7543	0.4044	1907.5	−3.23
		40	0.7480	0.3787	1987.0	−3.01
		50	0.7415	0.3309	1987.0	−3.01
		60	0.7341	0.2977	2066.5	−2.77

Table III. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m{}^*$ and Entropy of Activation $\Delta S_m{}^*$ for Data Points in the Miscible Region of the Ternary System *n*-Hexane (1)–Benzyl Alcohol (2)–Chlorobenzene (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m{}^*$, cal mol^{-1}	$\Delta S_m{}^*$, cal mol^{-1} K^{-1}
0.0474	0.3414	30	1.056	1.132	3815.0	+1.29
		40	1.052	0.9617	3338.2	−0.322
		50	1.047	0.8136	2861.3	−1.80
		60	1.042	0.7091	2384.4	−3.24
0.1127	0.4096	30	1.019	1.178	3974.0	+1.70
		40	1.016	0.9952	3656.1	+0.595
		50	1.009	0.8308	3338.2	−0.404
		60	1.006	0.7239	3020.2	−1.40
0.1630	0.2694	30	1.002	0.8984	3179.2	−0.405
		40	0.9974	0.7747	2940.8	−1.22
		50	0.9909	0.6496	2702.3	−1.91
		60	0.9865	0.5751	2463.9	−2.64
0.2158	0.5700	30	0.9607	1.406	4450.9	+2.87
		40	0.9549	1.178	3894.5	+0.963
		50	0.9489	0.9565	3338.2	−0.743
		60	0.9425	0.8219	2781.8	−2.44
0.2880	0.6464	30	0.9246	1.547	4768.8	+3.70
		40	0.9191	1.280	4212.4	+1.78
		50	0.9135	1.039	3735.6	+0.292
		60	0.9080	0.8869	3179.2	−1.43
0.3432	0.5019	30	0.9046	1.108	3974.0	+1.71
		40	0.8984	0.9399	3656.1	+0.588
		50	0.8928	0.7894	3338.2	−0.424
		60	0.8870	0.6849	3020.2	−1.42
0.3986	0.1543	30	0.8904	0.5826	2781.8	−0.981
		40	0.8876	0.5149	2463.9	−2.05
		50	0.8818	0.4551	2066.5	−3.29
		60	0.8765	0.4121	1748.6	−4.25
0.4780	0.2251	30	0.8545	0.6079	2861.3	−0.837
		40	0.8501	0.5389	2543.4	−1.93
		50	0.8427	0.4663	2225.4	−2.89
		60	0.8360	0.4176	1987.0	−3.61
0.5382	0.0684	30	0.8351	0.4615	2225.4	−2.42
		40	0.8274	0.4167	2145.9	−2.72
		50	0.8195	0.3667	2066.5	−2.94
		60	0.8140	0.3368	1987.0	−3.22

and drying, was rechecked by measuring their densities, viscosities, and refractive indices at 25 ± 0.1 °C. The mean of the values from several experiments agreed with the corresponding literature values within allowable limits (Table I) in each case. Redistilled, deionized, and degassed water showing electrical conductivity less than 7.0 × 10^{-7} mhos cm^{-1} was used for calibrating the pycnometers for density measurements.

Experimental Measurements. Ternary liquid mixtures in the miscible region of each system were prepared by weight as before (*3*, *4*) by using a chemical balance with an accuracy of 0.0001 g. For preparing ternary liquid mixtures saturated with an immiscible component, appropriate quantities of the pure liquids were taken in a thoroughly cleansed and dried separatory funnel and a closed rubber tube was put over its outlet to keep out the thermostat liquid. The separatory funnel was then placed in a thermostat set at 30 °C, with frequent shaking. After the contents came to equilibrium, sufficient time was permitted for complete phase separation. Then an ~ 0.3-μL sample (*6*, *7*) was withdrawn from the desired phase by using a microliter syringe and quickly injected in the column of a gas chromatograph for chromatographic analyses (*7*) of the phase composition. While samples from the heavier phase are withdrawn, the microsyringe, with its plunger down, was inserted quickly in it and small quantities of the mixture were

Table IV. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m^{\ddagger}$ and Entropy of Activation $\Delta S_m^{\ddagger}$ for Data Points in the Miscible Region of the Ternary System *n*-Hexane (1)–Benzyl Alcohol (2)–1-Hexanol (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m^{\ddagger}$, cal mol^{-1}	$\Delta S_m^{\ddagger}$, cal mol^{-1} K^{-1}
0.0534	0.3845	30	0.8840	3.165	8345.4	+13.9
		40	0.8809	2.493	6676.3	+8.22
		50	0.8773	1.853	5007.2	+2.97
		60	0.8729	1.476	3338.2	−2.07
0.1235	0.4489	30	0.8881	2.608	5166.2	+3.88
		40	0.8846	2.038	4689.3	+2.29
		50	0.8809	1.579	4212.4	+0.848
		60	0.8777	1.275	3735.6	−0.558
0.1819	0.3007	30	0.8464	2.145	4927.8	+3.42
		40	0.8434	1.705	4450.9	+1.82
		50	0.8386	1.324	4033.6	+0.583
		60	0.8344	1.097	3576.6	−0.803
0.2246	0.5933	30	0.9044	1.987	4530.4	+2.37
		40	0.9001	1.591	4371.4	+1.82
		50	0.8936	1.264	4132.9	+1.09
		60	0.8879	1.045	3974.0	+0.592
0.2915	0.6543	30	0.9129	1.754	4371.4	+2.13
		40	0.9084	1.426	3974.0	+0.795
		50	0.9016	1.132	3576.6	−0.385
		60	0.8955	0.9579	3179.2	−1.59
0.3532	0.5166	30	0.8657	1.369	3576.6	−0.077
		40	0.8611	1.137	3735.6	+0.413
		50	0.8558	0.9255	3815.1	+0.686
		60	0.8510	0.7902	3974.0	+1.11
0.4342	0.1680	30	0.7787	1.025	3576.6	+0.357
		40	0.7736	0.8529	3656.1	+0.586
		50	0.7674	0.7016	3656.1	+0.596
		60	0.7619	0.5821	3735.6	+0.852
0.5055	0.2381	30	0.7807	0.8589	3179.2	−0.584
		40	0.7774	0.7324	3099.7	−0.865
		50	0.7706	0.6099	3059.9	−0.948
		60	0.7644	0.5224	3020.2	−1.06
0.5799	0.0739	30	0.7377	0.6861	3815.0	+1.90
		40	0.7314	0.5799	3179.2	−0.222
		50	0.7258	0.5029	2384.4	−2.73
		60	0.7208	0.4490	1748.6	−4.65

sucked in and released after short intervals several times in order to avoid any contamination with the lighter phase. All precautions were taken to obtain sharp chromatograms and a standard technique (*8*) was adopted to determine the component concentrations of the samples from the peak areas. Component concentrations, so determined, when plotted on a triangular composition diagram, represent a data point on the binodal curve (*9*) for the corresponding ternary system. A CIC India Model AC 1-TC gas chromatograph was used.

A thoroughly cleansed, dried, and calibrated Ostwald viscometer was used for viscosity measurements and the experimental procedure adopted remained the same as described elsewhere (*1–5*, *10*). Care was taken to keep the viscometer limbs vertical within 0.5° and limit the standard deviation for the time of flow within 0.1%. A Weld-type pycnometer of capacity about 25 mL was employed for density measurements (*10*), and distilled conductivity grade water with 0.99707 g mL^{-1} as its density at 25 °C was used as reference liquid for calibration.

All the experimental measurements were carried out in a Toshniwal GL-15 precision thermostat. Bath temperatures were set and monitored to 0.01 °C with a Beckmann thermometer which had been standardized with a certified thermometer. For each measurement, sufficient time was allowed for thermal equilibrium to be attained and care was taken to minimize evaporation and limit the fluctuation in bath temperature within ±0.1 °C. The measured viscosities and densities were considered significant to four figures.

Table V. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m^{\ddagger}$ and Entropy of Activation $\Delta S_m^{\ddagger}$ for Data Points in the Miscible Region of the Binary System *n*-Hexane (1)–Benzyl Alcohol (2) at Different Temperatures

X_1	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m^{\ddagger}$, cal mol^{-1}	$\Delta S_m^{\ddagger}$, cal mol^{-1} K^{-1}
Binary Rich in Benzyl Alcohol					
0.0000	30	1.043	4.609	5394.7	+3.74
	40	1.034	3.328		
	50	1.027	2.539		
	60	1.019	1.997		
0.0312	30	1.026	4.044	5098.2	+2.97
	40	1.018	3.013		
	50	1.011	2.360		
	60	1.004	1.852		
0.0645	30	1.011	3.832	4967.5	+2.71
	40	1.004	2.754		
	50	0.9965	2.173		
	60	0.9888	1.712		
0.0976	30	0.9965	3.350	4922.7	+2.75
	40	0.9893	2.394		
	50	0.9816	1.974		
	60	0.9743	1.594		
0.1313	30	0.9826	3.119	4813.5	+2.58
	40	0.9751	2.256		
	50	0.9675	1.790		
	60	0.9603	1.465		
0.1653	30	0.9679	2.649	4490.6	+1.77
	40	0.9602	2.004		
	50	0.9529	1.616		
	60	0.9462	1.349		
0.2056	30	0.9506	2.328	4126.2	0.790
	40	0.9434	1.827		
	50	0.9362	1.455		
	60	0.9282	1.291		
0.2550[a]	30	0.9295	1.972	3665.7	−0.429
	40	0.9225	1.615		
	50	0.9176	1.327		
	60	0.9126	1.113		
Binary Rich in *n*-Hexane					
0.8792[a]	30	0.6984	0.3644	1399.6	−4.84
	40	0.6899	0.3351		
	50	0.6805	0.3066		
	60	0.6710	0.2825		
0.9550	30	0.6733	0.3264	1630.6	−3.89
	40	0.6650	0.3024		
	50	0.6556	0.2680		
	60	0.6458	0.2456		
0.9699	30	0.6684	0.3195	1562.1	−4.072
	40	0.6600	0.2996		
	50	0.6505	0.2619		
	60	0.6407	0.2381		
0.9799	30	0.6648	0.3115	1541.6	−4.103
	40	0.6571	0.2915		
	50	0.6472	0.2575		
	60	0.6374	0.2365		
0.9899	30	0.6620	0.3034	1456.7	−4.337
	40	0.6535	0.2835		
	50	0.6439	0.2541		
	60	0.6340	0.2330		
1.0000	30	0.6588	0.2935	1358.4	−4.603
	40	0.6502	0.2735		
	50	0.6405	0.2505		
	60	0.6305	0.2301		

[a] Binary saturated at 30 °C.

Results and Discussion

Experimental viscosity–composition–temperature data for mixture compositions in the miscible region at 30, 40, 50, and 60 °C are listed in Tables II–V. Similar data for mixture compositions which fall on the binodal curves at 30 °C and in the miscible region at 40, 50 and 60 °C are listed in Tables

Table VI. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m^{\ddagger}$ and Entropy of Activation $\Delta S_m^{\ddagger}$ for Data Points Which Fall on the Binodal Curve at 30 °C and in the Miscible Region at 40, 50, and 60 °C of the Ternary System *n*-Hexane (1)–Benzyl Alcohol (2)–Toluene (3)

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m^{\ddagger}$, cal mol^{-1}	$\Delta S_m^{\ddagger}$, cal mol^{-1} K^{-1}
0.3306	0.6043	30	0.8855	1.443	4371.4	+2.48
		40	0.8770	1.198	3735.6	+0.347
		50	0.8715	0.9889	3199.1	−1.32
		60	0.8640	0.8373	2543.4	−3.28
0.4672	0.4288	30	0.8270	0.9325	3854.8	+1.58
		40	0.8207	0.0121	3179.2	−0.726
		50	0.8135	0.6923	2384.4	−3.20
		60	0.8059	0.6163	1748.6	−5.12
0.6099	0.2755	30	0.7691	0.5872	6517.4	+11.2
		40	0.7617	0.5200	4212.4	+3.38
		50	0.7526	0.4609	2384.4	−2.48
		60	0.7417	0.4311	556.4	−8.08
0.6954	0.2093	30	0.7455	0.5186	2702.3	−1.16
		40	0.7386	0.4553	2265.2	−2.60
		50	0.7302	0.4103	1748.6	−4.24
		60	0.7224	0.3730	1430.6	−5.20
0.8267	0.1429	30	0.6974	0.3656	2384.4	−1.60
		40	0.6894	0.3302	1589.6	−4.22
		50	0.6818	0.3023	1072.9	−5.82
		60	0.6733	0.2833	794.8	−6.66
0.2883	0.6944	30	0.9277	1.734	3576.6	−0.429
		40	0.9195	1.489	3497.1	−0.785
		50	0.9116	1.215	3417.6	−1.00
		60	0.9034	1.019	3338.2	−1.23
0.8149	0.1215	30	0.7072	0.3932	3497.1	+1.95
		40	0.6994	0.3423	2066.5	−2.73
		50	0.6906	0.3163	1231.9	−5.38
		60	0.6838	0.2977	1112.7	−5.76
0.2722	0.6929	30	0.9234	1.713	3974.0	+0.887
		40	0.9206	1.430	3735.6	+0.053
		50	0.9132	1.203	3576.6	−0.482
		60	0.9055	1.006	3417.6	−0.958
0.7576	0.1544	30	0.7236	0.4752	2821.5	−0.598
		40	0.7172	0.4181	2781.8	−0.785
		50	0.7129	0.3705	2622.8	−1.34
		60	0.7047	0.3192	2543.4	−1.56
0.3124	0.6201	30	0.9049	1.474	4609.8	+3.26
		40	0.8973	1.265	3894.5	+0.79
		50	0.8900	1.076	3576.6	−0.292
		60	0.8829	0.8599	3536.9	−0.316

VI–VIII. In order to calculate the free energy of activation, $\Delta G^{\ddagger}$, of the viscous flow in a liquid mixture, the Eyring equation was used in the following form

$$\eta_m = (hN/V_m)\exp(\Delta G_m^{\ddagger}/RT) \qquad (1)$$

with

$$V_m = \sum X_i M_i/\rho_m \qquad (2)$$

$$\Delta G_m^{\ddagger} = \Delta H_m^{\ddagger} - T\Delta S_m^{\ddagger} \qquad (3)$$

where ρ_m is the mixture density at T K, M_i is the molecular weight of the mixture component i, while $\Delta H_m^{\ddagger}$ and $\Delta S_m^{\ddagger}$ are the enthalpy and the entropy of activation of viscous flow, respectively. The remaining symbols have been defined earlier. Incorporating eq 3 in eq 1 and plotting ln $(\eta_m V_m)$ against $1/T$ for each ternary system studied, it was found that the plots show a curvature which indicates that $\Delta H_m^{\ddagger}$ values are not altogether temperature-invariant. As such, the $\Delta H_m^{\ddagger}(T)$ values were obtained from the slopes of the curves at corresponding T. However, in the case of the partially miscible binary system *n*-hexane (1)–benzyl alcohol (2), similar ln $(\eta_m V_m)$ vs. $1/T$ plots are linear, showing that $\Delta H_m^{\ddagger}$ as calculated from the corresponding slope for this system is constant in the temperature range studied. The value of $\Delta H_m^{\ddagger}$ so obtained, together with

Table VII. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m^{\ddagger}$ and Entropy of Activation $\Delta S_m^{\ddagger}$ for Data Points Which Fall on the Binodal Curve at 30 °C and in the Miscible Region at 40, 50, and 60 °C of the Ternary System *n*-Hexane (1)–Benzyl Alcohol (2)–Chlorobenzene (3)

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m^{\ddagger}$, cal mol^{-1}	$\Delta S_m^{\ddagger}$, cal mol^{-1} K^{-1}
0.3883	0.5499	30	0.8742	1.267	6080.2	+8.35
		40	0.8669	0.9706	5007.2	+4.79
		50	0.8594	0.7899	3974.0	+1.49
		60	0.8518	0.6677	2861.3	−1.90
0.5568	0.3535	30	0.8075	0.7191	4530.4	+4.27
		40	0.8009	0.5931	3874.7	+2.07
		50	0.7931	0.5034	3179.2	−0.167
		60	0.7850	0.4249	2543.4	−2.05
0.5578	0.3624	30	0.8066	0.7949	4768.8	+4.86
		40	0.7992	0.6113	3974.0	+2.32
		50	0.7912	0.5285	3338.2	+0.232
		60	0.7825	0.4502	2702.3	−1.69
0.7731	0.1831	30	0.7308	0.4645	3815.0	+2.68
		40	0.7235	0.3808	2702.3	−0.902
		50	0.7152	0.3400	2225.4	−2.43
		60	0.7074	0.3036	2066.5	−2.91
0.3494	0.6171	30	0.9019	1.443	3974.0	+1.02
		40	0.8992	1.204	3735.6	+0.361
		50	0.8932	0.9997	3656.1	+0.102
		60	0.8851	0.8254	3576.6	−0.113
0.8088	0.1590	30	0.7111	0.3982	3020.2	−0.162
		40	0.7039	0.3498	2781.8	−0.505
		50	0.6954	0.3194	2503.6	−1.49
		60	0.6879	0.2820	1589.6	−4.23
0.2841	0.6933	30	0.9207	1.699	3894.5	+0.615
		40	0.9153	1.397	3815.0	+0.327
		50	0.9093	1.159	3735.6	+0.061
		60	0.9016	0.9345	3616.3	−0.232

Table VIII. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation $\Delta H_m^{\ddagger}$ and Entropy of Activation $\Delta S_m^{\ddagger}$ for Data Points Which Fall on the Binodal Curve at 30 °C and in the Miscible Region at 40, 50, and 60 °C of the Ternary System *n*-Hexane (1)–Benzyl Alcohol (2)–1-Hexanol (3)

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	$\Delta H_m^{\ddagger}$, cal mol^{-1}	$\Delta S_m^{\ddagger}$, cal mol^{-1} K^{-1}
0.4718	0.4837	30	0.8280	1.035	4927.8	+4.88
		40	0.8213	0.8179	4013.7	+1.98
		50	0.8132	0.7286	3179.2	−0.869
		60	0.8046	0.6039	2384.4	−3.20
0.5203	0.4189	30	0.8057	0.9024	5007.2	+5.39
		40	0.7994	0.7245	3854.8	+1.60
		50	0.7918	0.6234	3179.2	−0.589
		60	0.7835	0.5181	2543.4	−2.45
0.3379	0.6289	30	0.8853	1.565	5881.5	+7.28
		40	0.8776	1.219	4768.8	+3.59
		50	0.8707	0.9930	3735.6	+0.312
		60	0.8627	0.8321	2702.3	−2.81
0.6549	0.3011	30	0.7599	0.6612	4768.8	+5.16
		40	0.7521	0.5387	3576.6	+1.24
		50	0.7439	0.4663	2583.1	−1.92
		60	0.7355	0.4045	1828.0	−4.17
0.7579	0.2197	30	0.7395	0.5275	3179.2	+0.362
		40	0.7339	0.4627	2861.3	−0.743
		50	0.7256	0.4004	2702.3	−1.26
		60	0.7170	0.3482	2702.3	−1.25
0.3599	0.6106	30	0.8600	1.342	5325.2	+5.70
		40	0.8545	1.041	4291.9	+2.34
		50	0.8473	0.8626	3735.6	+0.545
		60	0.8409	0.7149	3417.6	−0.396
0.8353	0.1581	30	0.6867	0.3752	3020.2	+0.403
		40	0.6791	0.3273	2384.4	−1.71
		50	0.6703	0.2896	1847.9	−3.38
		60	0.6609	0.2581	1669.1	−3.88
0.3001	0.6751	30	0.9133	1.729	4927.8	+3.98
		40	0.9066	1.427	4192.6	+1.48
		50	0.9005	1.199	3179.2	−1.72
		60	0.8935	1.004	3417.6	−0.977

the $\Delta G_m^{\ddagger}$ values calculated by eq 1 were then used to calculate the corresponding $\Delta S_m^{\ddagger}$ by using eq 3. Also, the nonlinearity of the ln $(\eta_m V_m)$ vs. $1/T$ plots suggests that the mechanism of viscous flow involves more than one thermally activated process whereas in the case of the binary subsystem *n*-hexane (1)–benzyl alcohol (2), the viscous flow is a single thermally activated process as indicated by the linear ln $(\eta_m V_m)$ vs. $1/T$ plots. The results as included in Tables II–VIII show that $\Delta H_m^{\ddagger}$ values are all positive and decrease with the increase of temperature while $\Delta S_m^{\ddagger}$ values are positive at 30 °C in most cases, show a decreasing trend with increasing temperature, and ultimately become negative.

These trends are similar to those observed for completely miscible ternary systems reported earlier (*1–5*) and support the suggestion that sufficient number of alcohol monomers are not available in these ternaries at lower temperature in order to facilitate the viscous flow via activated state of the monomeric molecular species, resulting in comparatively higher values of $\Delta S_m^{\ddagger}$. However, as the temperature increases, an increase in alcoholic monomers due to breaking of H bonds in the system studied leads to more disorder and consequently higher entropy of unactivated molecular species in comparison to activated ones giving lower $\Delta S_m^{\ddagger}$ which ultimately become negative at sufficiently higher temperature. Thus for the ternary system *n*-hexane (1)–benzyl alcohol (2)–1-hexanol (3) with two alcoholic components, mixture compositions having $(X_2 + X_3) > 0.9$, which are expected to have comparatively more increased H bonding and lesser availability of monomeric species, should give comparatively much higher $\Delta S_m^{\ddagger}$. Actually this is the case with a ternary mixture of *n*-hexane (1)–benzyl alcohol (2)–1-hexanol (3) having $(X_2 + X_3) = 0.9466$ which gives $\Delta S_m^{\ddagger} = 13.9$ cal mol^{-1} K^{-1}, a much higher value in comparison to other ternaries with lesser total alcoholic concentration.

Glossary

$\Delta G^{\ddagger}$	free energy of activation of viscous flow
$\Delta H^{\ddagger}$	enthalpy of activation of viscous flow
$\Delta S^{\ddagger}$	entropy of activation of viscous flow
h	Planck's constant
M	molecular weight
n_D	refractive index
N	Avogadro's number
R	universal gas constant
V	molar volume, cm^3 mol^{-1}
X	mole fraction

Greek Letters

η	absolute viscosity, cP
ρ	density, g mL^{-1}

Subscripts

i	component in a mixture
m	mixture
1, 2, 3	component number in a mixture

Registry No. *n*-Hexane, 110-54-3; toluene, 108-88-3; benzyl alcohol, 100-51-6; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3.

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