Table III. Values of the Corresponding Constants in Eq 1 and Standard Deviation, σ, for All Six Binary Mixtures

T/K	a_0[a]	a_1[a]	a_2[a]	σ[a]
Nitrobenzene + 1,2-Dichloroethane				
303.15	−0.0554	−0.0978	−0.0004	0.003
313.15	−0.1261	−0.0285	0.0325	0.001
Nitrobenzene + 1,1,1-Trichloroethane				
303.15	−2.0968	0.2374	−0.3635	0.002
313.15	−2.4991	0.5716	0.0674	0.003
Nitrobenzene + 1,1,2,2-Tetrachloroethane				
303.15	−0.5235	0.1492	0.1447	0.003
313.15	−0.5863	0.1525	0.2363	0.003

[a] Units: cm mol^{-1}.

excess quantities were fitted by the method of least squares by using the polynomial form

$$V^{E} = x_A(1 - x_A) \sum_{n=0} a_i(2x_A - 1)^i \qquad (1)$$

The coefficients a_i and the corresponding standard deviations are given in Table III. The solid curves in Figures 1 and 2, which give plots of V^E vs. mole fraction x_A, were calculated by using these coefficients. The measured V^E data at 303.15 and 313.15 K for nitrobenzene with chloroethanes are presented by the points in Figures 1 and 2.

Acknowledgment

K.D.R. is thankful to University authorities for providing the necessary facilities.

Registry No. Nitrobenzene, 98-95-3; 1,2-dichloroethane, 107-06-2; 1,1,1-trichloroethane, 71-55-6; 1,1,2,2-tetrachloroethane, 79-34-5.

Literature Cited

(1) Rao, M. V. P.; Naidu, P. R. *J. Chem. Thermodyn.* **1976**, *8*, 96.
(2) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1976**, *54*, 2280.
(3) Reddy, S. S.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 173.
(4) Karunakar, J.; Reddy, K. D.; Rao, M. V. P. *J. Chem. Eng. Data* **1982**, *27*, 346.
(5) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(6) Storkey, D. J.; Sallak, H. M.; Smith, B. D. *J. Chem. Thermodn.* **1973**, *5*, 741.
(7) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1965.
(8) Dreisbach, R. R. "Physical Properties of Chemical Compounds"; American Chemical Society: Washington, DC, 1955 and 1957.

Received for review September 23, 1983. Revised manuscript received April 23, 1984. Accepted May 18, 1984.

Viscosities and Activation Energies of Viscous Flow of the Ternary Mixtures of *n*-Hexane, Toluene, Chlorobenzene, and 1-Hexanol

Ramesh P. Singh* and Chandreshwar P. Sinha[†]
Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur, India

Mixture viscosities and the densities of the ternary mixtures of *n*-hexane, toluene, chlorobenzene, and 1-hexanol were measured at 30, 40, 50, and 60 °C over the complete composition range. The experimental viscosity–composition–temperature data were compared with those calculated from an equation based on the significant liquid structure theory. Activation enthalpies and entropies for viscous flow have been obtained and their variations with composition have also been discussed.

Introduction

Considering the usefulness of the predictions of mixture viscosities with the help of pure-component data as input, our earlier work (*1*) on the binary mixtures of *n*-hexane with toluene, chlorobenzene, and 1-hexanol was extended to ternary mixtures. In this paper, we report the viscosities and activation energies of viscous flow of the title ternaries at different temperatures and include the comparison of the experimental data with those predicted by an equation based on significant liquid structure theory (SLS) using only pure-component parameters.

Experimental Section

Materials. *n*-Hexane, toluene, and chlorobenzene were BDH (India) chemicals, procured from Glaxo Laboratories (India) Ltd., Bombay, while 1-hexanol was a BDH (England) chemical, procured from BDH Chemicals Ltd., Poole, England. These chemicals were further purified by fractional distillation and drying. Experimentally determined densities, viscosities, and refractive indices of these liquids checked within allowed limits with the corresponding literature values (Table I).

The water used for checking the instruments and calibrating the pycnometers for density measurements was redistilled and deionized till it showed an electrical conductivity of <7.0 × 10^{-7} mho cm^{-1}. Before calibration, the dissolved air was expelled from the water used.

Experimental Measurements. Ternary liquid mixtures were prepared by weight in a chemical balance with an accuracy of 0.0001 g, using certified weights. The procedure remained the same as that followed in the case of binary mixtures (*1*, *2*), and, knowing the component weights, we calculated the exact compositions. The experimental determinations were carried out by using required volumes of the same stock solution. Ostwald viscometers used for viscosity measurements were thoroughly cleansed, dried, and calibrated in each case. Errors due to alignment and loading of viscometers were minimized by taking proper precautionary measures such that the viscometer limbs coincided with the vertical within 0.5° and the standard deviations for time of flow were well within 0.1%. The experimental procedure adopted for viscosity measurements was the same as that described elsewhere (*3*).

Densities were determined pycnometrically (*3*) by using distilled conductivity-grade water with 0.997 07 as its density at 25 °C for calibration. The pycnometer used in the experiments was of weld type (volume, 25 mL; and capillary diameter, <1 × 10^{-4} m).

In each case, viscosity and density measurements using the same stock solution were carried out in a Toshniwal GL-15 precision thermostat allowing sufficient time for attaining thermal equilibrium and minimizing evaporation. Bath temperatures

---

[†] Present address: Department of Chemistry, Ananda Chandra College, Jalpaiguri 735101, West Bengal, India.

0021-9568/85/1730-0038$01.50/0

Table I. Density, Refractive Index, and Viscosity of Pure Components of Ternaries Selected

chemical	ρ, g mL^{-1}		n		η, cP	
	measd at 25 ± 0.1 °C	std 25 °C	measd at 25 ± 0.1 °C	std 25 °C	measd at 25 ± 0.1 °C	std 25 °C
n-hexane	0.6549	0.654 81[a]	1.372 25	1.372 26[a]	0.299	0.2985[a]
toluene	0.8623	0.862 31[a]	1.494 15	1.494 13[a]	0.552	0.5516[a]
chlorobenzene	1.1011	1.101 10[b]	1.521 65	1.521 60[c]	0.758	0.7580[b]
1-hexanol	0.8161	0.815 90[a]	1.416 11	1.416 10	4.59	4.5920[a]

[a] Reference *12*. [b] Reference *13*. [c] Reference *14*.

Table II. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation ΔH_m^* and Entropy of Activation ΔS_m^* for the Ternary Mixture n-Hexane (1)–Toluene (2)–Chlorobenzene (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	ΔH_m^*, cal mol^{-1}	ΔS_m^*, cal mol^{-1} K^{-1}
0.0484	0.5975	30	0.9327	0.5960	2861.28	–0.63
		40	0.9264	0.5234	2384.40	–2.21
		50	0.9191	0.4611	1987.00	–3.44
		60	0.9144	0.4192	1510.12	–4.87
0.1144	0.4638	30	0.9323	0.5698	2622.84	–1.34
		40	0.9271	0.5087	2225.44	–2.68
		50	0.9191	0.4489	1907.52	–3.65
		60	0.9141	0.4083	1589.60	–4.60
0.1615	0.5544	30	0.8860	0.5257	2622.84	–1.22
		40	0.8812	0.4725	2145.96	–2.82
		50	0.8765	0.4175	1748.56	–4.03
		60	0.8682	0.3837	1271.68	–5.47
0.2161	0.2050	30	0.9416	0.5455	2304.92	–2.34
		40	0.9345	0.4917	2145.96	–2.90
		50	0.9314	0.4415	1987.06	–3.39
		60	0.9260	0.4005	1828.04	–3.87
0.2862	0.0623	30	0.9406	0.5378	2384.40	–2.07
		40	0.9366	0.4834	2066.50	–3.13
		50	0.9321	0.4317	1748.60	–4.11
		60	0.9268	0.3954	1430.64	–5.06
0.3430	0.1481	30	0.8968	0.4991	2066.48	–3.00
		40	0.8913	0.4499	1907.52	–3.53
		50	0.8821	0.4001	1748.60	–4.00
		60	0.8810	0.3707	1510.12	–4.73
0.4056	0.4351	30	0.8055	0.4299	2384.40	–1.72
		40	0.8003	0.3860	2066.48	–2.78
		50	0.7920	0.3449	1828.04	–3.52
		60	0.7876	0.3157	1510.12	–4.48
0.4827	0.2867	30	0.8006	0.4119	2145.96	–2.45
		40	0.7969	0.3694	1987.00	–2.98
		50	0.7861	0.3348	1748.56	–3.74
		60	0.7820	0.3098	1589.60	–4.24
0.5470	0.3824	30	0.7562	0.3785	2225.44	–2.06
		40	0.7522	0.3468	1907.52	–3.14
		50	0.7466	0.3135	1589.60	–4.13
		60	0.7379	0.2871	1271.68	–5.08

Table III. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation ΔH_m^* and Entropy of Activation ΔS_m^* for the Ternary Mixture n-Hexane (1)–Chlorobenzene (2)–1-Hexanol (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	ΔH_m^*, cal mol^{-1}	ΔS_m^*, cal mol^{-1} K^{-1}
0.0503	0.6492	30	0.9772	0.9411	3576.60	+0.75
		40	0.9722	0.8137	3179.20	–0.62
		50	0.9659	0.6774	2781.80	–1.81
		60	0.9590	0.5974	2384.40	–3.03
0.1212	0.5138	30	0.9267	0.9725	3974.00	+1.93
		40	0.9214	0.8380	3576.60	+0.53
		50	0.9158	0.6907	3179.20	–0.68
		60	0.9111	0.6008	2781.80	–1.91
0.1709	0.5951	30	0.9383	0.7570	3179.20	–0.17
		40	0.9355	0.6646	2781.80	–1.52
		50	0.9294	0.5669	2384.40	–2.72
		60	0.9245	0.5053	1987.00	–3.92
0.23.2	0.2374	30	0.8349	1.1349	3974.00	+1.51
		40	0.8292	0.9558	3576.60	+0.15
		50	0.8243	0.7724	3179.20	–1.02
		60	0.8209	0.6656	2781.80	–2.22
0.3240	0.0737	30	0.7838	1.2667	4768.80	+3.85
		40	0.7787	1.0379	4371.40	+2.46
		50	0.7733	0.8279	3974.00	+1.24
		60	0.7667	0.6993	3576.60	–0.01
0.3755	0.1695	30	0.7958	0.8837	3974.00	+1.97
		40	0.7910	0.7591	3576.60	+0.57
		50	0.7834	0.6182	3179.20	–0.62
		60	0.7760	0.5381	2781.80	–1.85
0.4095	0.4593	30	0.8631	0.5329	2781.80	–0.85
		40	0.8570	0.4789	2225.40	–2.72
		50	0.8483	0.4184	1798.60	–4.01
		60	0.8420	0.3810	1192.20	–5.83
0.4972	0.3088	30	0.8091	0.5305	3179.30	+0.40
		40	0.8037	0.4772	2622.80	–1.51
		50	0.7940	0.4145	2066.50	–3.24
		60	0.7870	0.3691	1589.60	–4.65
0.5446	0.3980	30	0.8231	0.4434	2384.40	–1.83
		40	0.8186	0.4020	1987.00	–3.17
		50	0.8082	0.3558	1589.60	–4.38
		60	0.8028	0.3255	1192.20	–5.56

were set and monitored to 0.01 °C with a Beckmann thermometer which had been standardized with a certified thermometer. The fluctuations in the bath temperature were always within ±0.1 °C.

The repeat viscosity measurements showed uncertainties in the fourth decimal place for the ternaries rich in n-hexane, toluene, and chlorobenzene and in the third decimal place for those rich in 1-hexanol. The uncertainty for repeat density measurements entered into the fourth decimal place in each case.

Results and Discussion

The experimental viscosity–composition–temperature data for the title ternary liquid mixtures are presented in Tables II–V, which exclude the pure-component η–T data as the same have been presented in an earlier communication (*1*). In order to represent the dependence of viscosity on composition in liquid mixtures, equations based on McAllister type three-body interactions have been used by several workers (*4–6*) in the past. Recently an equation incorporating four-body interactions was used more favorably by Noda et al. (*7*). But all such equations involve several adjustable parameters which need mixture data for their evaluation. In view of this, an equation which is based on the SLS concept and, in comparison to equations based on simple algebraic mixing rules, gives satisfactory predictions of binary mixture viscosities (*1*) in certain cases was extended to ternary liquid mixtures, giving

$$\eta_m = \frac{Nh}{r_m}\,\frac{6}{2^{1/2}}\,\frac{1}{(1-e^{-\theta_1/T})^{X_1}}\,\frac{1}{(1-e^{-\theta_2/T})^{X_2}} \times \frac{1}{(1-e^{-\theta_3/T})^{X_3}}\,\frac{1}{V_m - V_{sm}}\exp\left[\frac{a_m E_{sm} V_{sm}}{RT(V_m - V_{sm})}\right] + \frac{V_m - V_{sm}}{V_m}\left[\frac{2}{3{d_1}^2}\left(\frac{m_1 kT}{\pi^3}\right)^{1/2} X_1 + \frac{2}{3{d_2}^2}\left(\frac{m_2 kT}{\pi^3}\right)^{1/2} X_2 + \frac{2}{3{d_3}^2}\left(\frac{m_3 kT}{\pi^3}\right)^{1/2} X_3\right] \quad (1)$$

Table IV. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation ΔH_m^* and Entropy of Activation ΔS_m^* for the Ternary Mixture *n*-Hexane (1)–Toluene (2)–1-Hexanol (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	ΔH_m^*, cal mol^{-1}	ΔS_m^*, cal mol^{-1} K^{-1}
0.0518	0.6389	30	0.8321	0.7697	3179.20	−0.23
		40	0.8271	0.6579	2781.80	−1.52
		50	0.8220	0.5508	2384.40	−2.70
		60	0.8167	0.4848	1987.00	−3.87
0.1240	0.5027	30	0.8151	0.8347	3974.00	+2.19
		40	0.8084	0.7029	3576.60	+0.83
		50	0.8039	0.5851	3179.20	−0.40
		60	0.7977	0.5119	2781.80	−1.64
0.1754	0.5843	30	0.8084	0.6348	3974.00	+2.75
		40	0.8020	0.5476	3338.20	+0.58
		50	0.7957	0.4671	2622.79	−1.67
		60	0.7890	0.4136	1987.01	−3.59
0.2417	0.2294	30	0.7863	1.0379	4768.81	+4.29
		40	0.7804	0.8545	4132.91	+2.13
		50	0.7744	0.7089	3417.53	−0.14
		60	0.7682	0.6068	2781.81	−2.07
0.3250	0.0708	30	0.7665	1.2164	5166.20	+5.23
		40	0.7599	0.9864	4371.40	+2.55
		50	0.7531	0.7990	3576.62	+0.05
		60	0.7470	0.6699	2781.82	−2.33
0.3783	0.1634	30	0.7606	0.8204	3576.60	+0.79
		40	0.7545	0.6853	3179.18	−0.52
		50	0.7480	0.5803	2781.78	−1.75
		60	0.7420	0.5023	2384.42	−2.93
0.4178	0.4482	30	0.7619	0.4791	3576.62	+1.94
		40	0.7572	0.4098	2781.80	−0.68
		50	0.7506	0.3603	1987.00	−3.18
		60	0.7450	0.3328	1192.20	−5.61
0.5040	0.2994	30	0.7424	0.5093	3576.58	+1.76
		40	0.7361	0.4371	3020.20	−0.11
		50	0.7299	0.3741	2543.42	−1.59
		60	0.7237	0.3445	1987.02	−3.55
0.5542	0.3874	30	0.7365	0.4098	3576.62	+2.21
		40	0.7297	0.3519	2781.82	−0.42
		50	0.7233	0.3124	1987.02	−2.94
		60	0.7169	0.2916	1192.20	−5.39

where η is the absolute viscosity, V is the molar volume, V_s is the solidlike volume in V, θ is the Einstein characteristic temperature, E_s is the energy of sublimation, m is the mass of a single molecule with diameter d in the gaseous state, and a is determined by another parameter n whereas r is equal to the product of the number of nearest neighbors Z and the transmission coefficient κ. Since it is difficult to determine the values of Z a priori and evaluate κ theoretically, r is treated as a disposable parameter and is usually fixed by forcing agreement between experimental and calculated viscosities at each temperature.

The mixture parameters, namely, r_m, E_{sm}, V_m, V_{sm}, and a_m, were calculated from corresponding pure-component parameters by using suitable mixture rules (*8*, *9*) in the form of the following equations:

$$r_m = X_1^2 r_1 + X_2^2 r_2 + X_3^2 r_3 + 2X_1X_2r_{12} + 2x_2X_3r_{23} + 2X_3X_1r_{31} \qquad (2)$$

$$E_{sm} = X_1^2 E_{s_1} + X_2^2 E_{s_2} + X_3^2 E_{s_3} + 2X_1X_2E_{s_{12}} + 2X_2X_3E_{s_{23}} + 2X_3X_1E_{s_{31}} \qquad (3)$$

$$V_m = X_1V_1 + X_2V_2 + X_3V_3 \qquad (4)$$

$$V_{sm} = X_1V_{s_1} + X_2V_{s_2} + X_3V_{s_3} \qquad (5)$$

$$a_m = X_1a_1 + X_2a_2 + X_3a_3 \qquad (6)$$

with the values of

$$r_{ij} = (r_ir_j)^{1/2}$$

$$E_{s_{ij}} = (E_{s_i}E_{s_j})^{1/2}$$

Table V. Experimental Densities ρ_m and Viscosities η_m and Corresponding Values of the Enthalpy of Activation ΔH_m^* and Entropy of Activation ΔS_m^* for the Ternary Mixture Toluene (1)–Chlorobenzene (2)–1-Hexanol (3) at Different Temperatures

X_1	X_2	t, °C	ρ_m, g mL^{-1}	η_m, cP	ΔH_m^*, cal mol^{-1}	ΔS_m^*, cal mol^{-1} K^{-1}
0.0614	0.6417	30	0.9916	0.9776	3576.62	+0.70
		40	0.9860	0.8351	3179.20	−0.65
		50	0.9800	0.7074	2781.82	−1.87
		60	0.9746	0.6198	2384.38	−3.07
0.1455	0.4997	30	0.9554	1.039	4132.90	+2.38
		40	0.9491	0.8811	3576.62	+0.48
		50	0.9439	0.7335	3020.18	−1.24
		60	0.9379	0.6349	2384.38	−3.16
0.2027	0.5723	30	0.9804	0.8483	3974.00	+2.31
		40	0.9738	0.7344	3179.20	−0.38
		50	0.9677	0.6298	2384.38	−2.86
		60	0.9634	0.5571	1589.60	−5.23
0.2795	0.2248	30	0.8846	1.2419	4291.92	+2.48
		40	0.8788	1.029	3815.00	+0.86
		50	0.8747	0.8439	3338.20	−0.60
		60	0.8694	0.7163	2781.82	−2.27
0.3715	0.0686	30	0.8474	1.338	4530.40	+3.08
		40	0.8420	1.094	3974.00	+1.22
		50	0.8372	0.8903	3417.60	−0.50
		60	0.8338	0.7498	2781.82	−2.40
0.4259	0.1559	30	0.8728	1.035	4371.40	+3.12
		40	0.8668	0.8731	3815.02	+1.21
		50	0.8618	0.7226	3338.20	−0.28
		60	0.8573	0.6258	2781.82	−1.99
0.4610	0.4192	30	0.9511	0.6997	3338.20	+0.61
		40	0.9446	0.6165	2781.82	−1.28
		50	0.9395	0.5335	2225.40	−3.00
		60	0.9340	0.4830	1589.60	−4.93
0.5496	0.2766	30	0.9151	0.7127	3576.62	+1.33
		40	0.9085	0.6203	2861.30	−1.07
		50	0.9033	0.5357	2225.40	−3.04
		60	0.8975	0.4853	1589.60	−4.97
0.5960	0.3531	30	0.9409	0.6264	2781.82	−0.99
		40	0.9342	0.5559	2384.38	−2.33
		50	0.9292	0.4919	1987.00	−3.56
		60	0.9230	0.4557	1589.60	−4.80

Table VI. Values of Physical Properties and Parameters Used in Eq 1 for the Ternary Components

parameter	t, °C	*n*-hexane	toluene	chlorobenzene	1-hexanol	ref
E_s, cal mol^{-1}		10022.00	9517.00	11019.00	15480.00	*10*
θ		62.10	103.62	105.41	74.67	*10*
n		10.9982	11.3269	11.3531	11.2653	*10*
10^3a		3.168	1.434	1.322	1.708	*10*
10^8d, cm		5.179	4.915	4.868	4.988	*10*
r	30	1.426	0.7359	0.7425	0.1864	
	40	1.485	0.7598	0.8016	0.2342	
	50	1.556	0.8502	0.8888	0.3076	
	60	1.612	0.9355	0.9632	0.3952	

The required values of V, V_s, M, E_s, θ, a, n, d, and r for the pure components as input data were taken from an earlier work (*1*, *2*, *10*) and are listed in Table VI.

The ternary mixture viscosities as calculated by eq 1 were compared with the corresponding experimental mixture viscosities. The root mean square (rms) deviations as recorded in Table VII clearly show that eq 1 can safely be employed to predict the viscosity–composition–temperature data for the ternary liquid mixtures studied without using experimental mixture viscosities. The mean rms deviations for *n*-hexane (1)–toluene (2)–chlorobenzene (3), *n*-hexane (1)–chlorobenzene (2)–1-hexanol (3), *n*-hexane (1)–toluene (2)–1-hexanol (3), and toluene (1)–chlorobenzene (2)–1-hexanol (3), in the temperature range studied, are 0.0266, 0.0524, 0.7435, and 0.0828, respectively, with an overall average of 0.0591 for all the systems taken together. It may also be pointed out that the deviations

Table VII. Root Mean Square (rms) Deviations for Different Ternary Systems Using the SLS Equation (1) at Different Temperatures

ternary system	rms deviation by eq 1[a] 30 °C	40 °C	50 °C	60 °C	mean
n-hexane (1)–toluene (2)–chlorobenzene (3)	0.0194	0.0297	0.0280	0.0294	0.0266
n-hexane (1)–chlorobenzene (2)–1-hexanol (3)	0.0524	0.0437	0.0558	0.0576	0.0524
n-hexane (1)–toluene (2)–1-hexanol (3)	0.0536	0.0718	0.0867	0.0853	0.0744
toluene (1)–chlorobenzene (2)–1-hexanol (3)	0.0585	0.0834	0.0953	0.0951	0.0828
					0.0591 (overall mean)

[a] rms deviation = $[\sum d_i^2/n]^{1/2}$ where n is the number of observations and d = (exptl − calcd)/exptl.

for the ternaries studied (Table VII) were found to be of the same order as those for the corresponding binary subsystems reported earlier (*1*).

Further, the free energies of activation of the viscous flow were calculated by using the Eyring viscosity equation (*11*)

$$\eta_m = (hN/V_m)\exp[\Delta G_m{}^*/RT] \qquad (7)$$

where $\Delta G_m{}^*$ is the free energy of activation of the viscous flow, R is the gas constant, and T is the absolute temperature, while V_m was calculated from the corresponding mixture density values by using the following relation:

$$V_m = \frac{\sum X_i M_i}{\rho_m} \qquad (8)$$

$$\Delta G_m{}^* = \Delta H_m{}^* - T\Delta S_m{}^* \qquad (9)$$

Here ρ_m is the mixture density, M_i is the molecular weight of pure component i, $\Delta H_m{}^*$ is the enthalpy of activation, and $\Delta S_m{}^*$ is the entropy of activation of viscous flow. Incorporating eq 9 into eq 7 and plotting ln $(\eta_m V_m)$ against $1/T$ for each ternary liquid mixture, we found that the plots show a curvature which indicates that $\Delta H_m{}^*$ values are not constant in the temperature range investigated. As such, the individual $\Delta H_m(T)$ values were obtained from the slopes of the curves at corresponding T. The $\Delta H_m{}^*$ values so obtained together with $\Delta G_m{}^*$ values calculated by eq 7 were then used to calculate the corresponding $\Delta S_m{}^*$ by using eq 9. The results are listed in Tables II–V. In view of the fact that the plots of ln $(\eta_m V_m)$ vs. $1/T$ are nonlinear (Figure 1), it is suggested that the mechanism of viscous flow for the ternaries studied is not a thermally activated single process unlike in the case of their binary subsystems which give linear ln $(\eta_m V_m)$ vs. $1/T$ plots (*1*). The values of $\Delta H_m{}^*$, as determined, are all positive and decrease with increasing temperature in each case, while $\Delta G_m{}^*$ values are all positive and decrease with increasing temperature for ternaries rich in 1-hexanol, whereas for the rest the trend is reversed. As regards $\Delta S_m{}^*$ values, these are positive at 30 °C, decrease with increasing temperature, and ultimately become negative in the case of the ternaries having considerable proportion of 1-hexanol. In all other cases, these are negative and as before decreases with increasing temperature.

The above observations suggest that the formation of activated species necessary for viscous flow in the ternaries significantly deficient in 1-hexanol leads to increased molecular order which is enhanced with the increase in temperature. On the other hand, the situation for the ternaries with considerable proportion of 1-hexanol is different. At low temperature not many 1-hexanol monomers are available and the H-bonded network has to be broken to some extent for facilitating the viscous flow via activated state of the molecular species. Consequently, the overall molecular order, in this case, is decreased, giving positive $\Delta S_m{}^*$. But for the same ternaries, at higher temperatures, the availability of randomly scattered 1-hexanol monomers is sufficient for the formation of activated molecular species which lead to increased order as a result of viscous flow giving negative $\Delta S_m{}^*$.

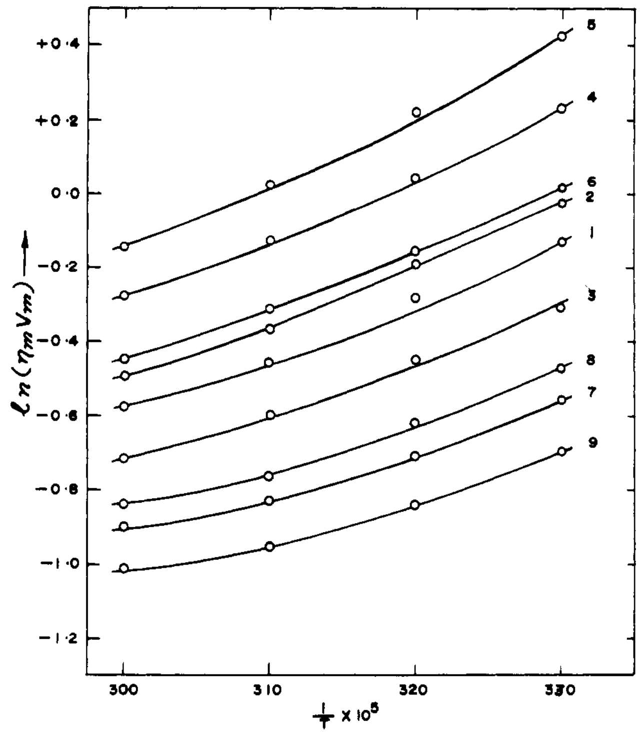

Figure 1. Plots of ln $(\eta_m V_m)$ vs. $1/T$ for the ternary mixture *n*-hexane (1)–toluene (2)–1-hexanol (3): (1) $X_1 = 0.0518$, $X_2 = 0.6389$; (2) $X_1 = 0.1240$, $X_2 = 0.5027$; (3) $X_1 = 0.1754$, $X_2 = 0.5843$; (4) $X_1 = 0.2417$, $X_2 = 0.2294$; (5) $X_1 = 0.3250$, $X_2 = 0.0708$; (6) $X_1 = 0.3783$, $X_2 = 0.1634$; (7) $X_1 = 0.4178$, $X_2 = 0.4432$; (8) $X_1 = 0.5040$, $X_2 = 0.2994$; (9) $X_1 = 0.5542$, $X_2 = 0.3874$.

Acknowledgment

We are grateful to the authorities of the Bhagalpur College of Engineering, Bhagalpur, for providing laboratory facilities.

Glossary

a	adjustable parameter
d	diameter in gaseous state
d	deviation
E_s	energy of sublimation
ΔG^*	free energy of activation of viscous flow
ΔH^*	enthalpy of activation of viscous flow
ΔS^*	entropy of activation of viscous flow
h	Planck's constant
M	molecular weight
m	mass of a single molecule
N	Avogadro's number
n	refractive index
V	molar volume, cm^3 mol^{-1}
V_s	solidlike volume in V, cm^3 mol^{-1}
X	mole fraction

Greek Letters

η	absolute viscosity, centipoise
θ	Einstein characteristic temperature
κ	transmission coefficient

ρ	density

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; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3.

Literature Cited

(1) Singh, R. P.; Sinha, C. P. *J. Chem. Eng. Data*, in press.
(2) Singh, R. P.; Sinha, C. P. *J. Chem. Eng. Data* **1982**, *27*, 283.
(3) (a) Daniels, F.; Williams, J. W.; Bender, P.; Alberty, A. R. Cornwell, C. D.; Harriman, J. E. "Experimental Physical Chemistry", 6th ed.; McGraw-Hill-Kogakusha Book Co.: New York, 1970; p 164. (b) *Ibid.*, p 493. (c) *Ibid.*, p 193.
(4) Noda, K.; Ishida, K. *J. Chem. Eng. Jpn.* **1977**, *10*, 478.
(5) Kalidas, R.; Laddha, G. S. *J. Chem. Eng. Data* **1964**, *9*, 142.
(6) Heric, E. L. *J. Chem. Eng. Data* **1966**, *11*, 66.
(7) Noda, K.; Ohashi, M.; Ishida, K. *J. Chem. Eng. Data* **1982**, *27*, 326.
(8) Rice, P.; Teja, A. A. *Chem. Eng. Sci.* **1982**, *37*, 1675.
(9) Eyring, H.; John, M. S. "Significant Liquid Structures"; Wiley: New York, 1969.
(10) Singh, R. P.; Sinha, C. P. *Indian J. Chem., Sect. A* **1978**, *16*, 821.
(11) Erdey-Gruz, T. "Transport Phenomena in Aqueous Solutions"; Adam Hilger: London, 1974; p 93.
(12) Riddick, A.; Bunger, W. B. "Organic Solvents": Wiley-Interscience: New York, 1970; Vol. 2.
(13) Timmermans, J. "Physicochemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950.
(14) Marsden, C.; Seymour, M. "Solvent Guide", 2nd ed; Cleaver Hume Press: London, 1963.

Received for review November 21, 1983. Accepted July 12, 1984. We are grateful to the UGC, New Delhi, for the award of a research grant to C.P.S.

Dielectric Behavior of the Ternary Mixtures of *n*-Hexane, Toluene, Chlorobenzene, and 1-Hexanol

Ramesh P. Singh* and Chandreshwar P. Sinha[†]

Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur, India

Mixture dielectric constants ϵ_m were measured for the ternaries of *n*-hexane, toluene, chlorobenzene, and 1-hexanol at 30, 40, 50, and 60 °C. Also the values of ϵ_m were calculated by an equation based on significant liquid structure (SLS) theory using pure-component properties only for the ternaries studied. A comparison of the calculated and experimental data showed that the SLS equation can be safely employed to predict the dependence of ϵ_m on the composition and the temperature of the systems studied when no ternary or binary experimental ϵ_m data are available.

Introduction

In an earlier work (*1*), experimentally determined mixture dielectric constants were reported for the binaries of *n*-hexane with toluene, chlorobenzene, and 1-hexanol in the temperature range 30–60 °C. A comparison of the experimental data with those calculated by using the Frohlich equation (*2*) and an equation (*1*) based on significant liquid structure (*3*) (SLS) theory showed that the latter gave better results. As an extension to these studies, the present paper reports the measured dielectric constants of the ternary liquid mixtures formed by the same pure components at 30, 40, 50, and 60 °C and provides a comparison of the measured data with those calculated by the ternary form of the SLS equation. It may also be pointed out that the SLS equation (*1*) is applicable in the entire composition range of the liquid mixtures (*1*, *3–5*) involving polar or associated components as against certain simpler equations (*6*) which are satisfactory only in the dilute composition range.

Experimental Section

Liquid samples similar to those employed in our previous studies (*1*, *7*) were purified (*8*) by fractional distillation and drying before use. The density, viscosity, and refractive index of the purified samples as determined at 25 °C in each case and reported in the preceding paper (*7*) were in reasonable agreement with the corresponding values published in the literature (*1*).

Table I. Experimental Dielectric Constant ϵ_m for the Ternary System *n*-Hexane (1)–Toluene (2)–Chlorobenzene (3) at Different Temperatures

		ϵ_m			
X_1	X_2	30 °C	40 °C	50 °C	60 °C
0.0484	0.5975	3.235	3.214	3.183	3.130
0.1144	0.4638	3.386	3.349	3.132	3.276
0.1665	0.5544	2.927	2.906	2.870	2.849
0.2161	0.2050	3.823	3.782	3.724	3.678
0.2862	0.0623	3.927	3.891	3.849	3.777
0.3430	0.1481	3.464	3.443	3.396	3.359
0.4056	0.4351	2.463	2.448	2.432	2.406
0.4827	0.2867	2.568	2.547	2.536	2.505
0.5470	0.3824	2.145	2.135	2.125	2.109

Experimental Measurements

Ternary mixtures were prepared by weighing the desired pure components with an accuracy of 0.0001 g in a chemical balance using certified weights. The procedure remained the same as that followed in the case of binary mixtures (*1*, *9*), and, knowing the component weights, we calculated the exact compositions. Mixture dielectric constants of the same stock solution (*7*) were measured at 30, 40, 50, and 60 °C as described elsewhere (*1*) by using a Toshniwal dipolemeter type RL 09 working on the heterodyne beat principle. In each case, the cell temperature was maintained by circulating thermostated water from a temperature bath whose temperature was monitored to 0.01 °C with a standardized Beckmann thermometer. The accuracy of measured mixture dielectric constants was found to be within 2% at 30, 40, and 50 °C whereas it was considered within 3% for the measurements at 60 °C. The molar volumes (*1*) as calculated from the measured densities were considered significant to four figures (*1*) whereas required refractive indices were obtained at desired temperatures from smoothened literature data significant to five figures (*8*, *10*, *11*).

[†] Present address: Department of Chemistry, Ananda Chandra College, Jalpaiguri 735101, West Bengal.

0021-9568/85/1730-0042$01.50/0