Viscosities and Activation Energies of Viscous Flow of Ternary Mixtures of Toluene, Chlorobenzene, 1-Hexanol, and Benzyl Alcohol

Ramesh P. Singh* and Chandreshwar P. Sinha†

Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur 813210, India

Mixture viscosities and the densities of the ternary mixtures of toluene, chlorobenzene, 1-hexanol, and benzyl alcohol were measured at 30, 40, 50, and 60 °C. 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

Recently, we reported (*1–6*) viscosities and dielectric constants of several binary and ternary liquid mixtures at various temperatures. As an extension of that work, we have measured densities and viscosities of the ternary mixtures of toluene, chlorobenzene, 1-hexanol, and benzyl alcohol at 30, 40, 50, and 60 °C.

Experimental Section

Materials. Toluene, chlorobenzene, 1-hexanol, and benzyl alcohol, all of BDH origin, were purified by fractional distillation and drying. For purity check, the densities, viscosities, and refractive indices of the pure liquids were measured at 25 ± 0.1 °C. The mean of several repeat measurements compared with the corresponding literature value within allowable limits (Table IV). Redistilled and deionized water which showed an electrical conductivity $<7.0 \times 10^{-7}$ mhos cm^{-1} was used for checking the instruments and calibrating the pycnometers for density measurements. Care was taken to expel all the dissolved air from the water used before calibration.

Experimental Measurements. Ternary liquid mixtures were prepared by weight in a chemical balance with an accuracy of 0.0001 g. Thoroughly cleansed, dried, and calibrated Ostwald viscometers were used for viscosity measurements. Necessary precautions were taken to ascertain that the viscometer limbs coincided with the vertical within 0.5° and the standard deviation for the time of flow in each case did not exceed 0.1%. The experimental procedure adopted for viscosity measurements was the same as described elsewhere (*7*).

Densities were determined pycnometrically (*7*) by using distilled conductivity grade water with 0.997 07 g mL^{-1} as its density at 25 °C 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 to attain thermal equilibrium and care was taken to minimize evaporation and limit the fluctuations in bath temperature within ±0.1 °C. The measured viscosities and densities were considered significant to four figures.

Results and Discussions

Tables I–III contain the experimental viscosity–composition–temperature data. In view of the success of an equation (*2, 4, 6*) based on significant liquid structure theory (SLS) of Eyring in predicting the binary mixture viscosities, the same was extended to ternary liquid mixtures giving

$$\eta_m = \frac{Nh}{r_m}\frac{6}{2^{1/2}}\frac{1}{(V_m - V_{sm})}\exp\left[\frac{a_m E_{sm} V_{sm}}{RT(V_m - V_{sm})}\right] \times \prod_i^3\left[\frac{1}{(1-\exp(-\theta_i/T)^{X_i}}\right] + \left(\frac{V_m - V_{sm}}{V_m}\right)\left[\sum_i^3 \frac{2}{3d_i^2}\left(\frac{m_i kT}{\pi^3}\right)^{1/2} X_i\right] \quad (1)$$

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 gaseous state, and a is determined (*8*) 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

Table I. 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)-Benzyl Alcohol (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}
0.0578	0.6045	30	1.0673	1.181	4371.4	+3.06
		40	1.0617	1.010	3576.6	+0.36
		50	1.0562	0.8335	2781.8	−2.08
		60	1.0522	0.7309	1987.0	−4.47
0.1355	0.4655	30	1.0460	1.309	4609.8	+3.64
		40	1.0404	1.098	3974.0	+1.46
		50	1.0349	0.8963	3338.2	−0.51
		60	1.0316	0.7736	2781.8	−2.21
0.1937	0.5468	30	1.0395	1.012	4768.8	+4.67
		40	1.0334	0.8545	3815.0	+1.45
		50	1.0280	0.7284	2940.8	−1.33
		60	1.0236	0.6341	1987.0	−4.20
0.2535	0.2039	30	1.0079	1.633	4768.8	+3.71
		40	1.0038	1.334	3974.0	+1.06
		50	0.9994	1.081	3179.2	−1.39
		60	0.9956	0.9105	2384.4	−3.74
0.3329	0.0614	30	0.9864	1.777	4768.8	+3.53
		40	0.9817	1.466	4132.9	+1.37
		50	0.9774	1.173	3417.6	−0.82
		60	0.9738	0.9912	2781.8	−2.66
0.3920	0.1434	30	0.9799	1.395	4768.8	+4.01
		40	0.9739	1.104	3974.0	+1.42
		50	0.9696	0.9121	3179.2	−1.06
		60	0.9654	0.7852	2384.4	−3.46
0.4499	0.4090	30	0.9830	0.7681	3179.2	−0.05
		40	0.9767	0.6742	2781.8	−1.41
		50	0.9720	0.5788	2384.4	−2.62
		60	0.9669	0.5137	2145.9	−3.33
0.5305	0.2670	30	0.9601	0.8112	3815.0	+1.93
		40	0.9549	0.7118	3020.2	−0.76
		50	0.9497	0.6009	2543.4	−2.21
		60	0.9443	0.5327	1987.0	−3.89
0.5898	0.3494	30	0.9547	0.6635	3179.2	+0.23
		40	0.9505	0.5942	2543.4	−1.92
		50	0.9439	0.5109	1987.0	−3.61
		60	0.9380	0.4609	1351.2	−5.51

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

0021-9568/85/1730-0470$01.50/0

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 Toluene (1)-1-Hexanol (2)-Benzyl Alcohol (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}
0.0650	0.5552	30	0.8959	3.124	5404.6	+4.30
		40	0.8913	2.451	5007.2	+2.94
		50	0.8871	1.862	4609.8	+1.75
		60	0.8852	1.491	4212.4	+0.56
0.1481	0.4156	30	0.9145	2.619	5722.6	+5.75
		40	0.9099	2.099	4927.8	+3.04
		50	0.9057	1.609	4371.4	+1.35
		60	0.9028	1.295	3576.6	−1.02
0.2152	0.4963	30	0.8841	2.242	5563.6	+5.50
		40	0.8795	1.775	4530.4	+2.07
		50	0.8753	1.370	3815.0	−0.09
		60	0.8722	1.117	2940.8	−2.67
0.2633	0.1730	30	0.9515	2.178	6119.9	+7.52
		40	0.9467	1.738	4927.8	+3.50
		50	0.9423	1.369	3735.6	−0.21
		60	0.9395	1.160	2622.8	−3.63
0.3367	0.0508	30	0.9692	1.947	5325.1	+5.16
		40	0.9643	1.576	4609.8	+2.73
		50	0.9601	1.259	3974.0	+0.74
		60	0.9573	1.047	3179.2	−1.66
0.4025	0.1203	30	0.9409	1.590	4927.8	+4.22
		40	0.9340	1.315	4212.4	+1.78
		50	0.9302	1.058	3576.7	−0.18
		60	0.9272	0.8948	2781.8	−2.57
0.4863	0.3611	30	0.8699	1.215	5404.6	+6.23
		40	0.8639	1.018	4371.4	+2.70
		50	0.8588	0.8255	3417.6	−0.28
		60	0.8538	0.7065	2384.4	−3.41
0.5578	0.2293	30	0.8860	1.089	4371.4	+3.08
		40	0.8806	0.9168	3815.0	+1.17
		50	0.8759	0.7539	3179.2	−0.79
		60	0.8729	0.6412	2622.8	−2.45
0.6301	0.3049	30	0.8567	0.8990	3974.4	+2.12
		40	0.8488	0.7571	3576.6	+0.75
		50	0.8443	0.6409	3179.2	−0.51
		60	0.8409	0.5545	2781.8	−1.72

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 Chlorobenzene (1)-1-Hexanol (2)-Benzyl Alcohol (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}
0.0678	0.5536	30	0.9105	3.344	5961.0	+6.01
		40	0.9062	2.543	5166.2	+3.38
		50	0.9020	1.910	4371.4	+0.97
		60	0.8994	1.545	3576.6	−1.41
0.1538	0.4128	30	0.9469	2.865	5563.6	+5.06
		40	0.9426	2.213	4768.8	+2.44
		50	0.9380	1.693	4371.4	+1.26
		60	0.9347	1.367	3974.0	+0.08
0.2229	0.4915	30	0.9316	2.415	5166.2	+4.06
		40	0.9270	1.914	4530.4	+1.94
		50	0.9225	1.486	4212.4	+0.99
		60	0.9187	1.205	3417.6	−1.37
0.2720	0.1709	30	1.013	2.349	4768.8	+2.93
		40	1.008	1.895	4371.4	+1.58
		50	1.003	1.480	3974.0	+0.39
		60	1.001	1.199	3576.6	−0.76
0.3467	0.0499	30	1.050	2.139	4768.8	+3.17
		40	1.044	1.721	4371.4	+1.82
		50	1.040	1.380	3974.0	+0.59
		60	1.037	1.158	3656.1	−0.40
0.4133	0.1181	30	1.035	1.818	4530.4	+2.68
		40	1.030	1.496	4132.9	+1.31
		50	1.025	1.196	3815.0	+0.35
		60	1.021	1.005	3179.2	−1.57
0.4974	0.3533	30	0.9792	1.487	5961.0	+7.71
		40	0.9739	1.189	4371.4	+2.43
		50	0.9687	0.9719	3417.6	−0.56
		60	0.9638	0.8123	2781.8	−2.44
0.5687	0.2236	30	1.015	1.302	3576.6	+0.15
		40	1.009	1.095	3179.2	−1.16
		50	1.005	0.9018	2781.8	−2.33
		60	1.001	0.7739	2384.4	−3.48
0.6405	0.2964	30	1.001	1.119	3179.2	−0.88
		40	0.9949	0.9485	3179.2	−0.90
		50	0.9899	0.7966	3179.2	−0.88
		60	0.9853	0.6844	3179.2	−0.88

value of Z a priori and evaluate κ theoretically, r is treated as disposable parameter and is usually fixed by forcing agreement between the 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 (*9*, *10*) in the following form

$$r_m = \sum_{i}^{3} X_i^2 r_i + \sum_{i \neq j}^{3} 2X_i X_j r_{ij} \quad (2)$$

$$E_{sm} = \sum_{i}^{3} X_i^2 E_{s_i} + \sum_{i \neq j}^{3} 2X_i X_j E_{s_{ij}} \quad (3)$$

$$V_m = \sum_{i}^{3} X_i V_i \quad (4)$$

$$V_{sm} = \sum_{i}^{3} X_i V_{s_i} \quad (5)$$

$$a_m = \sum_{i}^{3} X_i a_i \quad (6)$$

with the values of $r_{ij} = (r_i r_j)^{1/2}$ and $E_{s_{ij}} = (E_{s_i} E_{s_j})^{1/2}$.

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*, *6*) and are listed in Table IV.

The ternary mixture viscosities η_m were calculated by eq 1 and compared with the corresponding experimental values. The root mean square (rms) deviations, as recorded in Table V, clearly show that eq 1 can safely be employed to predict the viscosity–composition–temperature data within the experimental region studied for the title ternaries when no relevant binary or ternary experimental viscosities are readily available. The average rms deviations for toluene (1)–chlorobenzene (2)–benzyl alcohol (3), toluene (1)–1-hexanol (2)–benzyl alcohol (3), and chlorobenzene (1)–1-hexanol (2)–benzyl alcohol (3) in the temperature range studied are 0.0253, 0.0590, and 0.0489, respectively, with an overall average of 0.0444 for all the systems taken together. It may be pointed out here that more data points situated sufficiently close to each other in the corners of the composition triangles of the title ternaries are needed for better assessment of the applicability of eq 1 in such extreme regions.

In order to calculate the free energy of activation of the viscous flow, the Eyring viscosity equation (*11*) was used in the following form

$$\eta_m = (hN/V_m) \exp(\Delta G_m^{\ddagger}/RT) \quad (7)$$

where $\Delta G_m^{\ddagger}$ is the free energy of activation of the viscous flow, R is the gas constant, and T is temperature (K) while V_m was calculated from the corresponding mixture density values from the relation

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

$$\Delta G_m^{\ddagger} = \Delta H_m^{\ddagger} - T\Delta S_m^{\ddagger} \quad (9)$$

Here ρ_m is the mixture density, M_i is the molecular weight of

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

parameters	t, °C	toluene	chlorobenzene	1-hexanol	benzyl alcohol	ref
ρ, g mL^{-1}	25	0.8623 (0.86231)[a]	1.1011 (1.10110)[b]	0.8160 (0.81590)[a]	1.04129 (1.04127)[a]	
	30	0.86696	1.10003	0.81353	1.0419	
	40	0.85473	1.09394	0.81050	1.0386	
	50	0.84969	1.0888	0.8065	1.0350	
	60	0.8475	1.0839	0.8034	1.0315	
η, cP	25	0.552 (0.5516)[a]	0.758 (0.7580)[b]	4.59 (4.5920)[a]	4.648[e] (4.650)[a]	
	30	0.5372	0.7184	3.765	4.605	
	40	0.4851	0.6469	2.934	3.533	
	50	0.4272	0.5724	2.169	2.646	
	60	0.3905	0.5198	1.655	2.037	
n_D	25	1.49415 (1.49413)[a]	1.52165 (1.52160)[c]	1.41610 (1.41610)[a]	1.53840 (1.53837)[a]	
	30	1.4918	1.5194	1.4140	1.5349	
	40	1.4862	1.5143	1.4100	1.5321	
	50	1.4810	1.5092	1.4059	1.5281	
	60	1.4760	1.5045	1.4018	1.5241	
V_s, cm^3 mol^{-1}		89.53	89.50	110.4	94.80	*1, 6*
M		92.142	112.56	102.178	108.141	*12*
E_s, cal mol^{-1}		9517.0	11019.0	15480.0	16140.0	*2, 6*
θ, K		103.62	105.41	74.67	85.04	*2, 6*
n		11.3269	11.3531	11.2653	11.2857	*2, 6*
$a \times 10^3$		1.434	1.322	1.708	1.615	*2, 6*
$d \times 10^8$ cm		4.915	4.868	4.988	4.865	*2, 6*
r	30	0.7359	0.7425	0.1864	0.2638	*2, 6*
	40	0.7598	0.8016	0.2342	0.3310	*2, 6*
	50	0.8502	0.8888	0.3076	0.4251	*2, 6*
	60	0.9355	0.9632	0.3952	0.5330	*2, 6*

[a] Reference 12. [b] Reference 13. [c] Reference 14. [d] Reference 8. [e] At 30 °C.

Table V. Root Mean Square (rms) Deviations for Different Ternary Systems Using SLS Eq 1 at Different Temperatures

ternary systems	rms[a] deviation by eq 1				mean[b]
	30 °C	40 °C	50 °C	60 °C	
1. toluene (1)–chlorobenzene (2)–benzyl alcohol (3)	0.0328	0.0182	0.0236	0.0267	0.0253
2. toluene (1)–1-hexanol (2)–benzyl alcohol (3)	0.0358	0.0633	0.0690	0.0681	0.0590
3. chlorobenzene (1)–1-hexanol (2)–benzyl alcohol (3)	0.0223	0.0485	0.0614	0.0636	0.0489

[a] Rms deviation $[\sum d_i^2/n]^{1/2}$ where n is the number of observations and $d = [(\eta_{exptl} - \eta_{calcd})/\eta_{exptl}]$ where η values in cP. [b] Overall mean = 0.0444.

pure component i, $\Delta H_m^{\ddagger}$ is the enthalpy of activation, and $\Delta S_m^{\ddagger}$ is the entropy of activation of viscous flow. Incorporating eq 9 in eq 7 and plotting ln $(\eta_m V_m)$ against $1/T$ for each ternary liquid mixtures, it was found that the plots show a curvature which indicates that $\Delta H_m^{\ddagger}$ values are not constant in the temperature range investigated. As such, the $\Delta H_m^{\ddagger}(T)$ values were obtained from the slopes of the curves at corresponding T.

The values of $\Delta H_m^{\ddagger}$, so obtained, together with the $\Delta G_m^{\ddagger}$ values calculated by eq 7 were then used to calculate the corresponding $\Delta S_m^{\ddagger}$ by using eq 9. The results are listed in Table I–III. The nonlinearity of the plots of ln $(\eta_m V_m)$ vs. $1/T$ suggests that the mechanism of viscous flow for the ternaries studied involves more than one thermally activated process. In this connection it may be noted that the binary subsystems of each ternary studied gave linear ln $(\eta_m V_m)$ vs. $1/T$ plots (*2*) and accordingly the corresponding mechanism of viscous flow involved a single thermally activated process. An inspection of Tables I–III reveals that they are all positive and decrease with increasing temperature in each case. As regards $\Delta S_m^{\ddagger}$ values, these are positive at 30 °C in most of the cases, decrease with increasing temperature, and ultimately become negative.

The above observations suggest that sufficient number of benzyl alcohol monomers are not available in these ternaries at low temperature and H bonds have to be broken for facilitating the viscous flow via the activated state of the molecular species. Consequently the overall molecular order is decreased giving positive $\Delta S_m^{\ddagger}$. But, for the same system, at higher temperatures, the availability of randomly scattered benzyl alcohol monomers is sufficient for the formation of activated molecular species which then lead to comparatively increased order as a result of viscous flow giving negative $\Delta S_m^{\ddagger}$. This conclusion is in conformity with our results obtained in the case of the ternaries of *n*-hexane, toluene, chlorobenzene, and 1-hexanol communicated earlier (*2*).

Acknowledgment

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

Glossary

a	adjustable parameter
d	diameter in gaseous state, cm
d	deviation
E_s	energy of sublimation, cal mol^{-1}
$\Delta G^{\ddagger}$	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
m	mass of a single molecule
N	Avogadro's number
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, K
κ	transmission coefficient

Subscripts

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

Appendix

Sample Calculation for Mixture Viscosity by SLS Eq 1 by Using Hand Calculator.

Ternary Mixture: toluene (1)–chlorobenzene (2)–benzyl alcohol (3).

Composition: $X_1 = 0.2535$, $X_2 = 0.2039$, $X_3 = 0.5426$.

Temperature: 30 °C.

Pure component parameters: the values of r, ρ, M, V_s, a, E_s, θ, and d were taken from Table IV.

Constants: $N = 6.023 \times 10^{23}\ mol^{-1}$, $h = 6.625 \times 10^{-27}$ erg s. $k = 1.380 \times 10^{-16}$ erg deg^{-1}, $R = 1.987$ cal $deg^{-1}\ mol^{-1}$.

$$r_m = [(0.2535)^2 0.7359 + (0.2039)^2 0.7425 + (0.5426)^2 0.2638 + 2(0.2535)(0.2039)\{(0.7359)(0.7425)\}^{1/2} + 2(0.2039)(0.5426)\{(0.7425)(0.2638)\}^{1/2} + 2(0.2638)(0.2535)\{(0.2638)(0.7359)\}^{1/2}]$$

$$= 0.451\,405$$

$$E_{sm} = [(0.2535)^2 9517.0 + (0.2039)^2 11019.0 + (0.2638)^2 16140.0 + 2(0.2535)(0.2039)\{(9517.0)(11019.0)\}^{1/2} + 2(0.2039)(0.2638)\{(11019.0)(16140.0)\}^{1/2} + 2(0.2638)(0.2535)\{(16140.0)(9517.0)\}^{1/2}]$$

$$= 13\,243.5 \text{ cal mol}^{-1}$$

$$V_m = \sum_{i=1}^{3}[(X_i M_i)/\rho_i]$$

$$= \frac{(0.2535)(92.142)}{0.86696} + \frac{(0.2039)(112.56)}{1.10003} + \frac{(0.5426)(108.141)}{1.0419}$$

$$= 104.11 \text{ cm}^3 \text{ mol}^{-1}$$

$$V_{sm} = [(0.2535)(89.53) + (0.2039)(89.50) + (0.5426)(95.80)]$$

$$= 92.38 \text{ cm}^3 \text{ mol}^{-1}$$

$$a_m = [0.2535(1.434 \times 10^{-3}) + 0.2039(1.322 \times 10^{-3}) + 0.5426(1.615 \times 10^{-3})]$$

$$= 1.5094 \times 10^{-3}$$

$$A = \frac{Nh}{r_m}\frac{6}{2^{1/2}}\frac{1}{(V_m - V_{sm})} = \frac{(6.023 \times 10^{23})(6.625 \times 10^{-27})}{0.451405} \times \frac{6}{2^{1/2}}\frac{1}{(104.11 - 92.38)} = 3.1972 \times 10^{-3}\ P$$

$$B = \exp\left[\frac{a_m E_{sm} V_{sm}}{RT(V_m - V_{sm})}\right]$$

$$= \exp\left[\frac{(1.5094 \times 10^{-3})(13243.5)(92.38)}{(1.987)303.16(104.11 - 92.38)}\right]$$

$$= \exp[0.261347] = 1.298\,68$$

$$C = \prod_{i=1}^{3}\frac{1}{[1 - \exp(-\theta_i/T)]^{X_i}}$$

$$= \left[\frac{1}{[1 - \exp(-103.62/303.16)]^{0.2535}} \times \frac{1}{[1 - \exp(-105.41/303.16)]^{0.2039}} \times \frac{1}{[1 - \exp(-85.04/303.16)]^{0.5426}}\right]$$

$$= (1.36921)(1.28379)(2.14694) = 3.773\,85$$

$$D = (V_m - V_{sm})/V_m = (104.11 - 92.38)/104.11 = 0.112\,669$$

$$E = \sum_{i=1}^{3}\frac{2}{3d_i^2}\left(\frac{mkT}{\pi^3}\right)^{1/2} X_i = \sum_{i=1}^{3}\frac{2}{3d_i^2}\left(\frac{(M_i/N)kT}{\pi^3}\right)^{1/2} X_i$$

$$E = \frac{2}{3(4.915 \times 10^{-8})^2} \times \left[\frac{(92.142/6.023 \times 10^{23})(1.38 \times 10^{-16})(303.16)}{(3.14159)^3}\right]^{1/2} \times 0.2535 + \frac{2}{3(4.868 \times 10^{-8})^2} \times \left[\frac{(112.56/6.023 \times 10^{23})(1.38 \times 10^{-16})(303.16)}{(3.14159)^3}\right]^{1/2} \times 0.2039 + \frac{2}{3(4.885 \times 10^{-8})^2} \times \left[\frac{(108.14/6.023 \times 10^{23})(1.38 \times 10^{-16})(303.16)}{(3.14159)^3}\right]^{1/2} \times 0.5426$$

$$= (3.178 \times 10^{-5}) + (2.879 \times 10^{-5}) + (7.459 \times 10^{-5})$$

$$= 1.352 \times 10^{-4}\ P$$

$$\eta_m = (ABC) + (DE)$$

$$= [(3.1972 \times 10^{-3})(1.2987) \times (3.7739) + (0.112669 \times 1.352 \times 10^{-4})]$$

$$= 0.015\,685\ P = 1.569\ cP$$

$$\text{deviation} = (\eta_{exptl} - \eta_{calcd})/\eta_{exptl} = (1.633 - 1.569)/1.633 = 0.0392$$

Registry No. Toluene, 108-88-3; chlorobenzene, 108-90-7; 1-hexanol, 111-27-3; benzyl alcohol, 100-51-6.

Literature Cited

(1) Singh, R. P.; Sinha, C. P. *J. Chem. Eng. Data* **1982**, *27*, 283.
(2) Singh, R. P.; Sinha, C. P. *J. Chem. Eng. Data* **1985**, *30*, 38.
(3) Singh, R. P.; Sinha, C. P. *Indian J. Chem., Sect. A* **1982**, *21A*, 96.
(4) Singh, R. P.; Sinha, C. P. *Indian J. Chem., Sect. A* **1983**, *22A*, 282.
(5) Singh, R. P.; Sinha, C. P. *Z. Phys. Chem. (Leipzig)* **1982**, *263*, 1075.
(6) Singh, R. P.; Sinha, C. P. *Z. Phys. Chem. (Leipzig)* **1984**, *265*, 593.

(7) (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: New York, 1970; p 164. (b) *Ibid.* p 493. (c) *Ibid.* p 193.
(8) Singh, R. P.; Sinha, C. P. *Indian J. Chem., Sect. A* **1978**, *16*, 821.
(9) Rice, P.; Teja, A. S. *Chem. Eng. Sci.* **1982**, *37*, 1675.
(10) Eyring, H.; Jhon, M. S. "Significant Liquid Structure"; Wiley: New York, 1969.
(11) Erdey-Gruz, Tibor. "Transport Phenomena in Aqueous Solution"; Adam Hilger: London, 1974; p 93.
(12) Riddick, A.; Bunger, W. B. "Organic Solvents"; Wiley-Interscience: New York, 1970; Vol. 2.
(13) Timmermans, J. "Physico Chemical 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 March 23, 1984. Revised manuscript received November 16, 1984. Accepted January 28, 1985.

Dielectric Behavior of Ternary Mixtures of Toluene, Chlorobenzene, 1-Hexanol, and Benzyl Alcohol

Ramesh P. Singh* and Chandreshwar P. Sinha†

Department of Chemistry, Bhagalpur College of Engineering, Bhagalpur 813210, India

Mixture dielectric constants ϵ_m were measured for the ternaries of toluene, chlorobenzene, 1-hexanol, and benzyl alcohol 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 continuation of our earlier work (*1–5*) on the measurement and correlation of dielectric constants of liquid mixtures of varying nonideality, we report similar data for the ternary mixtures of toluene, chlorobenzene, 1-hexanol, and benzyl alcohol at 30, 40, 50, and 60 °C. The measured dielectric constant–composition–temperature data have been compared with those calculated by the ternary form of an equation based on the significant liquid structure (SLS) theory of Eyring.

Experimental Section

Materials. The samples of toluene, chlorobenzene, 1-hexanol, and benzyl alcohol (all BDH) were fractionally distilled and dried before use. The density, viscosity, and refractive index of the purified samples as determined at 25 ± 0.1 °C in each case and reported in the preceding paper (*6*) were in agreement with the corresponding values published in literature (*1*).

Table I. Experimental Dielectric Constant ϵ_m for the Ternary System Toluene (1)-Chlorobenzene (2)-Benzyl Alcohol (3) at Different Temperatures

		ϵ_m			
X_1	X_2	30 °C	40 °C	50 °C	60 °C
0.0578	0.6045	6.387	6.246	6.064	5.892
0.1355	0.4655	6.408	6.293	6.121	5.923
0.1937	0.5468	5.454	5.381	5.246	5.079
0.2535	0.2039	6.851	6.726	6.549	6.345
0.3329	0.0614	7.023	6.872	6.710	6.486
0.3920	0.1434	5.804	5.684	5.579	5.411
0.4499	0.4090	4.178	4.152	4.094	4.032
0.5305	0.2670	4.068	4.042	4.021	3.964
0.5898	0.3494	3.542	3.521	3.485	3.438

† Present Address: Department of Chemistry, Ananda Chandra College Jalpaiguri, W. Bengal, India.

Table II. Experimental Dielectric Constant ϵ_m for the Ternary System Toluene (1)-1-Hexanol (2)-Benzyl Alcohol (3) at Different Temperatures

		ϵ_m			
X_1	X_2	30 °C	40 °C	50 °C	60 °C
0.0650	0.5552	11.166	10.646	10.165	9.847
0.1481	0.4156	10.071	9.628	9.133	8.821
0.2152	0.4963	9.191	8.706	8.326	7.898
0.2633	0.1730	8.618	8.253	7.924	7.554
0.3367	0.0508	7.726	7.419	7.127	6.945
0.4025	0.1203	6.841	6.548	6.335	6.137
0.4863	0.3611	5.459	5.277	5.089	5.053
0.5578	0.2293	4.793	4.694	4.574	4.475
0.6301	0.3049	4.103	4.001	3.948	3.829

Table III. Experimental Dielectric Constant ϵ_m for the Ternary System Chlorobenzene (1)-1-Hexanol (2)-Benzyl Alcohol (3) at Different Temperatures

		ϵ_m			
X_1	X_2	30 °C	40 °C	50 °C	60 °C
0.0678	0.5536	11.515	10.879	10.399	9.941
0.1538	0.4128	10.529	9.988	9.613	9.253
0.2229	0.4915	9.811	9.248	8.915	8.649
0.2720	0.1709	9.628	9.154	8.852	8.602
0.3467	0.0499	8.946	8.581	8.326	8.128
0.4133	0.1181	8.341	7.992	7.700	7.482
0.4974	0.3533	7.252	7.002	6.783	6.579
0.5687	0.2236	6.841	6.695	6.549	6.424
0.6405	0.2964	6.293	6.168	6.048	5.955

Table IV. Values of Molar Volume, Dielectric Constant, and Adjustable Parameter G in SLS Equation and Dipole Moments for Selected Liquids

parameter	t, °C	toluene	chlorobenzene	1-hexanol	benzyl alcohol
V, cm^3 mol^{-1}	25	106.86 (106.85)[a]	102.23 (102.23)[b]	125.22 (125.23)[a]	103.85 (103.85)[a]
	30	106.3	102.3	125.6	103.8
	40	107.8	102.9	126.1	104.1
	50	108.4	103.4	126.7	104.5
	60	108.7	103.9	127.2	104.8
ϵ	25	2.416 (2.379)[a]	5.68 (5.621)[a]	13.4 (13.30)[a]	
	30	2.297	5.34	12.50	11.92
	40	2.281	5.27	11.46	11.02
	50	2.271	5.20	10.71	10.30
	60	2.260	5.10	10.09	9.81
G[c]	30	0.1951	0.2770	1.356	0.7255
	40	0.2118	0.2863	1.283	0.6908
	50	0.2444	0.2952	1.242	0.6635
	60	0.2752	0.2997	1.211	0.6526
μ, D		0.31[a]	1.54[a]	1.55[a]	1.66[a]

[a] Reference 8. [b] Reference 9. [c] Reference 1.

0021-9568/85/1730-0474$01.50/0