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

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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

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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.

Table V. Root Mean Square Deviations (rms) in SLS Equation Used in Prediction of Mixture Dielectric Constants

system	rms[a] deviation 30 °C	40 °C	50 °C	60 °C	av[b]
1. toluene (1)–chlorobenzene (2)–benzyl alcohol (3)	0.0832	0.0985	0.1069	0.1065	0.0988
2. toluene (1)–1-hexanol (2)–benzyl alcohol (3)	0.0811	0.1000	0.1103	0.1151	0.1016
3. chlorobenzene (1)–1-hexanol (2)–benzyl alcohol (3)	0.1079	0.0884	0.0757	0.0655	0.0844

[a] rms $= [\sum_{i=1}^{K}\{(\epsilon_{\text{exptl}} - \epsilon_{\text{calcd}})/\epsilon_{\text{exptl}}\}_i^2/K]^{1/2}$ where K is the number of data. [b] Overall average = 0.0949.

Experimental Measurements. Desired pure components were weighed with an accuracy of 0.0001 g in a sensitive chemical balance using certified weights and mixed in order to prepare ternary liquid mixtures. A Toshniwal dipolemeter Type RL 09 working on the heterodyne beat principle was used to measure the mixture dielectric constant data. The experimental procedure followed as described elsewhere (*1*). A thermostat whose bath temperature was monitored to 0.01 °C with a standardized Beckmann thermometer was used to circulate thermostated water around the cell containing experimental liquid mixture, and the temperature fluctuations in the cell did not exceed 0.1 °C. The measured dielectric constants were found accurate within 2% at 30, 40, and 50 °C and within 3% at 60 °C. The molar volumes as calculated from the measured densities (*7*) 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*).

Results and Discussion

The experimental dielectric constant–composition–temperature data for the title ternary mixtures are listed in Tables I–III. In order to carry out prediction calculations for ternary dielectric constants, the following ternary form of the (SLS) equation (*11*) was used

$$\frac{3\epsilon_m(\epsilon_m - n_m^2)}{(2\epsilon_m + n_m^2)} = \frac{4\pi N}{V_m}\left[\frac{\epsilon_m(n_m^2 + 2)}{(2\epsilon_m + n_m^2)}\right]^2\left[\frac{V_{sm}}{V_m}\left(\sum_i^3 \frac{X_i^2\mu_i^2G_i}{kT} + \sum_{i\neq j}^3 \frac{2X_iX_j\mu_i\mu_jG_{ij}}{kT}\right) + \frac{V_m - V_{sm}}{V_m}\left(\sum_i^3 \frac{X_i\mu_i^2}{3kT}\right)\right] \quad (1)$$

where ϵ is the dielectric constant, k is the Boltzmann constant, μ is the dipole moment of the free molecule, and V_s is the molar volume of the substance just before melting. The value of V_s was obtained by the method (*12*) described earlier.

The values of n_m, V_m, and V_{sm} can be given in terms of pure component properties and mole fraction X. When the following appropriate mixing equations (*11*, *13*) are used

$$V_m = \sum_i^3 X_iV_i \quad (2)$$

$$V_{sm} = \sum_i^3 X_iV_{s_i} \quad (3)$$

$$n_m = \sum_i^3 X_i^2 n_i + \sum_{i\neq j}^3 2X_iX_jn_{ij} \quad (4)$$

with $n_{ij} = (n_in_j)^{1/2}$ and $G_{ij} = (G_iG_j)^{1/2}$.

The subscript m stands for mixture and G is the correlation parameter. For each pure liquid, the value of G at each temperature was calculated by using an equation obtained by putting X_2 and X_3 = 0 and dropping the subscripts in eq 1. The values of V, μ, and G for the ternary components were taken from an earlier work (*1*, *4*) and are listed in Table IV, while the values of V_s and n were taken from the preceding paper (*6*).

The experimental ϵ_m–X–T data were compared with those predicted by eq 1. The root mean square (rms) deviations, as calculated in each case are listed in Table V. 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), the average of the rms derivatives in the temperature range investigated are 0.0988, 0.1016, and 0.0844, respectively, with an overall average of 0.0949 for all the systems taken together. This shows that eq 1 can be employed to predict tolerably ϵ_m–X–T data for the ternary mixtures in the experimental region studied utilizing only pure component data as input. However, for better assessment of the applicability of eq 1 in case of ternaries situated in the extreme corners of the composition triangle, more data points situated sufficiently close together in such regions are needed.

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Glossary

k	Boltzmann constant
n	refractive index
G	SLS correlation parameter (eq 1)
N	Avogadro's number
T	absolute temperature
V	molar volume at the temperature of investigation, $cm^3\ mol^{-1}$
V_s	molar volume of a substance just before melting, $cm^3\ mol^{-1}$
X_i	mole fraction of component i
rms	root mean square deviation
K	number of data

Greek Letters

ϵ	dielectric constant
μ	dipole moment of the free molecule, D

Subscripts

D	for sodium light
i, j	component in a mixture
m	mixture
1, 2, 3	component numbers in a mixture

Appendix

Sample Calculation for Mixture Dieletric Constant by SLS Eq 1 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 G, V, M, V_s, μ, and n_D were taken from Table IV and Table IV of preceding paper.

Constants: $N = 6.023 \times 10^{23}\ mol^{-1}$, $k = 1.38 \times 10^{-16}$ erg deg^{-1}.

In order to evaluate ϵ_m eq 1 is written in the form

$$2\epsilon_m^2 + L\epsilon_m + M = 0$$

Here $M = -n_m^4$, $L = -[n_m^2(1 + 4K/3) + (Kn_m^4/3) + 4K/3]$ where

$$K = \frac{4\pi N}{V_m}\left[\frac{V_{sm}}{V_m}\frac{1}{kT}\left(\sum_{i=1}^{3} X_i^2\mu_i^2 G_i + \sum_{i\neq j}^{3} 2X_iX_j\mu_i\mu_j(G_iG_j)^{1/2}\right) + \frac{V_m - V_{sm}}{V_m}\frac{1}{3kT}\left(\sum_{i=1}^{3} X_i\mu_i^2\right)\right]$$

$$n_m = [(0.2535)^2 1.4918 + (0.2039)^2 1.5194 + (0.5426)^2 1.5349 + 2(0.2535)(0.2039)\{(1.4918)(1.5194)\}^{1/2} + 2(0.2039)(0.5426)\{(1.5194)(1.5349)\}^{1/2} + 2(0.5426)(0.2535)\{(1.5349)(1.4918)\}^{1/2}]$$

$$= 1.5211$$

$$V_m = [(0.2535)(106.3) + (0.2039)(102.3) + (0.5426)(103.8)]$$

$$= 104.12 \text{ cm}^3 \text{ mol}^{-1}$$

$$V_{sm} = [(0.2535)(89.53) + (0.2039)(89.50) + (0.5426)(94.80)]$$

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

$$A = 4\pi N/V_m = 4(3.14159)(6.023 \times 10^{23})/104.12 = 7.269 \times 10^{22} \text{ cm}^{-3}$$

$$B = \frac{V_{sm}}{V_m}\frac{1}{kT} = \frac{92.38}{104.12}\frac{1}{(1.38 \times 10^{-16})303.16} = 2.1208 \times 10^{13} \text{ erg}^{-1}$$

$$AB = 1.5416 \times 10^{36}$$

$$C = AB\left(\sum_{i=1}^{3}(X_i^2\mu_i^2G_i)\right)$$

$$= (7.269 \times 10^{22})(2.1208 \times 10^{13})[(0.2535)^2(0.31 \times 10^{-18})^2(0.1951) + (0.2039)^2(1.54 \times 10^{-18})^2(0.2770) + (0.5426)^2(1.66 \times 10^{-18})^2(0.7255)]$$

$$= 1.5416 \times 10^{36}[6.1711 \times 10^{-37}] = 0.95134$$

$$D = AB\left(\sum_{i\neq j}^{3} 2X_iX_j\mu_i\mu_j(G_iG_j)^{1/2}\right)$$

$$= 1.5416 \times 10^{36}[2(0.2535)(0.2039)(0.31 \times 10^{-18})(1.54 \times 10^{-18})\{(0.1951)(0.2770)\}^{1/2} 2(0.2039)(0.5426)(1.54 \times 10^{-18}) \times (1.66 \times 10^{-18})\{(0.2770)(0.7255)\}^{1/2} 2(0.5426)(0.2535) \times (1.66 \times 10^{-18})(0.31 \times 10^{-18})\{(0.7255)(0.1951)\}^{1/2}]$$

$$D = 1.5416 \times 10^{36}[1.14729 \times 10^{-36} + 2.5358 \times 10^{-37} + 5.326 \times 10^{-38}]$$

$$= 1.5416 \times 10^{36}[3.18313 \times 10^{-37}] = 0.49071$$

$$E = \left(\frac{V_m - V_{sm}}{V_m}\right)\frac{1}{3kT} = \frac{(104.12 - 92.38)}{104.12}\,\frac{1}{3(1.38 \times 10^{-16})303.16}$$

$$= 8.9838 \times 10^{11} \text{ erg}^{-1}$$

$$F = AE\left(\sum_{i=1}^{3} X_i\mu_i^2\right)$$

$$= (7.269 \times 10^{22})(8.9838 \times 10^{11})[0.2535 \times (0.31 \times 10^{-18})^2 + 0.2039(1.54 \times 10^{-18})^2 + 0.5426 \times (1.66 \times 10^{-18})^2]$$

$$= (6.53032 \times 10^{34})[2.0031 \times 10^{-36}] = 0.13081$$

$$K = C + D + F$$

$$= 0.95134 + 0.49071 + 0.13081 = 1.57286$$

$$M = -n_m^4 = -(1.5211)^4 = -5.3534$$

$$L = -[(1.5211)^2(1 + \tfrac{4}{3}(1.57286)) + (1.57286/3) \times (1.5211)^4 + \tfrac{4}{3}(1.5729)]$$

$$= -12.0699$$

$$\epsilon_m = \frac{-L \pm (L^2 - 8M)^{1/2}}{2 \times 2} = \frac{-(-12.0699) + [(-12.0699)^2 - 8(-5.3534)]^{1/2}}{2 \times 2} = 6.4499$$

$$\text{deviation} = (\epsilon_{exptl} - \epsilon_{calcd})/\epsilon_{exptl} = (6.851 - 6.449)/6.851 = 0.0587$$

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

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