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

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Mixture dielectric constants ϵ_m were measured for the binaries of *n*-hexane with toluene, chlorobenzene, and 1-hexanol at 30, 40, 50, and 60 °C. Also the values of ϵ_m were calculated by using the Frohlich equation as well as an equation based on significant liquid structure (SLS) theory using pure-component properties only for the binaries studied. A comparison of the calculated and experimental data showed that the SLS equation gave better results than the Frohlich equation.

Introduction

The study of molecular systems by dielectric methods, which imply the nonquantal response to electric fields, is of considerable interest. On the stimulus first provided by Debye (*1*), the study of dielectric properties has since been actively and widely pursued. The earlier theories (*1*) neglect intermolecular forces and give satisfactory results only for gases at low pressures. As an improvement over Debye, Onsager (*2*) treated the molecules of a dielectric substance as a polarizable point dipole at the center of a spherical cavity of molecular dimensions in a continuous medium of static permittivity. Though his equation did not predict the occurrence of ferroelectricity, it avoids one of the assumptions which limit the validity of Debye's equation, namely, that the field due to the molecules in the spherical region is zero. It is, therefore, expected that Onsager's equation would apply to fluids but without the restriction on density to be expected for Debye's equation. Kirkwood (*3*) and later Frohlich (*4*) obtained expressions for dielectric constants using statistical methods throughout and avoiding the neglect of local forces which limit the validity of Debye's and Onsager's theories to fluids. Hobbs, Jhon, and Eyring (*5*) proposed a domain theory of H-bonded liquids introducing significant structure concepts and applied it successfully to water and various forms of ice. In order to assess the merits of the Frohlich treatment and the significant liquid structure (SLS) approach in predicting the dielectric behavior of binary liquid mixtures, it was considered appropriate to select such systems which varied considerably in nonideality because of distinctly differing liquid characteristics of their pure components.

Accordingly, *n*-hexane, toluene, chlorobenzene, and 1-hexanol were selected as representatives of apolar, weakly polar, nonassociating polar, and associating polar components, and the present paper provides experimental data on dielectric constants of the binaries *n*-hexane (1)–toluene (2), *n*-hexane (1)–chlorobenzene (2), and *n*-hexane (1)–1-hexanol (2) at different temperatures together with a comparison of the correlative ability of the mixture equations based on Frohlich's theory as well as on the significant liquid structure theory of Eyring and co-workers.

Experimental Section

n-Hexane, toluene, chlorobenzene, and 1-hexanol (all BDH) used were purified, whenever necessary, by suitable procedures involving fractional distillation and drying (*6*). The purity in each case was checked by the measurement of density, viscosity, and refractive index at 25 °C (Table I).

In order to prepare a binary mixture, pure components were taken separately in glass-stoppered bottles and thermostated at the desired temperature for a sufficient time. When the thermal equilibrium was ensured, the required volume of each component was weighted and transferred in a different bottle which was already thoroughly cleaned and dried. It was then stoppered, and the contents were shaken well and thermostated before use. In the preparation of different binaries, care was taken to ensure that the same procedure was adopted throughout the present work.

For dielectric measurements, the instrument employed was a Tosniwal type RL09 dipole meter which worked on the heterodyne beat principle. The values of the dielectric constants of the selected pure components and their binary mixtures at different temperatures were determined from a calibration curve which was obtained by plotting the dial readings of the dipole meter against the corresponding known dielectric constants. The temperature variations were limited to ±0.1 °C in each case. The experimental data on mixture dielectric constants ϵ_m for (i) the binaries of *n*-hexane–1-hexanol, except for a few, and (ii) the chlorobenzene-rich binaries of *n*-hexane–chlorobenzene were reported to three significant figures, whereas the rest were reported to four significant figures (Table II–IV). Further, on the basis of the comparison of literature values of the dielectric constant ϵ for *n*-hexane, toluene, and 1-hexanol with the corresponding measured values, the accuracy was found to be within 2%. However, for measurements near 60 °C, it was considered to be within 3%. The molar volumes V of each pure component at desired temperatures were obtained by measuring the corresponding densities with the help of a specific gravity bottle following the standard experimental procedure (*7*). The densities were considered significant to four figures, and the molecular weights used for calculating V were taken from the literature, as reported, significant to five figures. As such, the values of V were considered significant to four figures (Table V). The refractive indices n_D at the desired temperatures were obtained by extrapolation of a smooth curve obtained by plotting literature values (*6*, *8*, *9*) of n_D significant to five figures (Table V).

Results and Discussion

In order to correlate the dielectric constant data, the Frohlich equation for pure fluids was extended to consider the case of mixtures. If a mixture contains N_i molecules per unit volume of type i each of which consists of a polarizable point dipole of permanent moment μ_i and polarizability α_i and if the internal refractive index of the component is given by (*7*)

$$(n_i^2 - 1)/(n_i + 2) = \alpha_i/(\epsilon_0 a_i^3) \qquad (1)$$

where ϵ_0 is the permittivity of free space and a_i is the radius of the ith type of molecule and is related to ϕ_i by eq 2 (*10*),

$$\phi_i = 4\pi N_i a_i^3/3 \qquad (2)$$

then, assuming that the molecules fill the available space

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Table I. Density, Refractive Index, and Viscosity of Pure Components of the Binaries Studied

	density, gm mL^{-1}		refractive index		viscosity, cP	
chemical	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	0.8160	0.815 90[a]	1.416 10	1.416 10[a]	4.59	4.5920[a]

[a] Reference 6. [b] Reference 8. [c] Reference 9.

Table II. Experimental Dielectrical Constant ϵ_m for the Binary System n-Hexane (1)-Toluene (2) at Different Temperatures

	ϵ_m			
X_1	30 °C	40 °C	50 °C	60 °C
0.0	2.297	2.281	2.271	2.260
0.0826	2.271	2.255	2.239	2.229
0.1685	2.213	2.200	2.187	2.169
0.2578	2.172	2.161	2.145	2.127
0.3509	2.129	2.119	2.106	2.083
0.4477	2.088	2.078	2.059	2.041
0.5487	2.052	2.039	2.020	2.005
0.6541	2.013	1.999	1.981	1.968
0.7643	1.971	1.955	1.942	1.927
0.8795	1.927	1.916	1.903	1.890
1.0	1.890	1.879	1.869	1.859

Table III. Experimental Dielectric Constant ϵ_m for the Binary System n-Hexane (1)-Chlorobenzene (2) at Different Temperatures

	ϵ_m			
X_1	30 °C	40 °C	50 °C	60 °C
0.0	5.34	5.27	5.20	5.10
0.0793	5.00	4.95	4.91	4.87
0.1624	4.61	4.57	4.54	4.41
0.2494	4.28	4.23	4.18	4.13
0.3407	3.87	3.83	3.79	3.74
0.4367	3.532	3.495	3.459	3.427
0.5377	3.141	3.099	3.057	3.016
0.6440	2.786	2.760	2.750	2.708
0.7562	2.396	2.270	2.343	2.317
0.8747	2.083	2.057	2.031	2.005
1.0	1.890	1.879	1.869	1.859

Table IV. Experimental Dielectric Constant ϵ_m for the Binary System n-Hexane (1)-1-Hexanol (2) at Different Temperatures

	ϵ_m			
X_1	30 °C	40 °C	50 °C	60 °C
0.0	12.50	11.46	10.71	10.09
0.0954	10.74	10.12	9.55	9.24
0.1918	9.13	8.32	8.52	8.30
0.2892	7.78	7.65	7.54	7.45
0.3876	6.07	5.97	5.85	5.80
0.4870	4.80	4.65	4.49	4.34
0.5874	3.71	3.65	3.58	3.52
0.6890	2.78	2.77	2.76	2.75
0.7915	2.41	2.40	2.38	2.36
0.8952	2.03	2.01	1.99	1.98
1.0	1.890	1.879	1.869	1.859

Table V. Values of Molar Volume, Refractive Index, V_s, Dipole Moment, and Molecular Weight for Selected Liquids

parameters	temp, °C	n-hexane	toluene	chloro-benzene	1-hexanol
V, cm^3 mol^{-1}	30	130.9	106.3	102.3	125.6
	40	132.2	107.8	102.9	126.1
	50	133.9	108.4	103.4	126.7
	60	135.5	108.7	103.9	127.2
n_D,[a-c]	30	1.3699	1.4918	1.5194	1.4140
	40	1.3642	1.4862	1.5143	1.4100
	50	1.3589	1.4810	1.5092	1.4059
	60	1.3540	1.4760	1.5045	1.4018
V_s, cm^3 mol^{-1}		104.3[d]	89.53[d]	89.50[d]	110.4[d]
μ, D		0.085[a]	0.31[a]	0.31[a]	1.55[a]
M		86.178[a]	92.142[a]	112.56[a]	102.178[a]

[a] Reference 6. [b] Reference 8. [c] Reference 9. [d] Reference 12.

Table VI. Values of Adjustable Parameters g in Frohlich Equation and G in SLS Equation for Selected Liquids at Different Temperatures

para-meter	temp, °C	n-hexane	toluene	chloro-benzene	1-hexanol
g	30	2.382	0.6497	0.8509	3.687
	40	3.512	0.6964	0.8759	3.491
	50	4.492	0.7785	0.8996	3.372
	60	5.314	0.8558	0.9128	3.285
G	30	0.9118	0.1951	0.2770	1.356
	40	1.399	0.2118	0.2863	1.283
	50	1.829	0.2444	0.2952	1.242
	60	2.207	0.2752	0.2997	1.211

completely as is done in Onsager's theory such that ϕ_i gives the volume fraction of the ith species under the condition $\sum\phi_i = 1$, the Frohlich equation for mixtures takes the following form (*10*):

$$\sum\phi_i\frac{(\epsilon_m - n_i^2)}{(2\epsilon_m + n_i^2)} = \frac{1}{\epsilon_0}\sum\frac{\epsilon_m(n_i^2 + 2)^2}{3(2\epsilon_m + n_i^2)^2}\,\frac{4\pi n_i' g\mu^2}{3kT} \tag{3}$$

Here ϵ_m is the mixture dielectric constant, g is the correlation parameter, μ is the dipole moment of the free molecule, and n_i' is the number of molecules per unit volume of the mixture of components i and is given by

$$n_i' = \phi_i N/V_i \tag{4}$$

If one changes n_i and V_i to n_m and V_m for the mixture, taking them along with ϵ_m out of the summation sign and rearranging, eq 3 for binary mixtures reduces to

$$\frac{(\epsilon_m - n_m^2)(2\epsilon_m + n_m^2)}{3\epsilon_m}\,\frac{V_m}{4\pi N}\left(\frac{3}{n_m^2 + 2}\right)^2\epsilon_0 = \frac{\phi_1 g_1\mu_1^2}{3kT} + \frac{\phi_2 g_2\mu_2^2}{3kT} \tag{5}$$

In eq 5, the values of μ are those obtained in the gaseous phase and n_m and V_m can be given in terms of pure-component properties and mole fraction X as an approximation by (*11*)

$$n_m \simeq X_1^2 n_1 + 2X_{12}(n_1 n_2)^{1/2} + X_2^2 n_2 \tag{6}$$

$$V_m \simeq X_1 V_1 + X_2 V_2 \tag{7}$$

Also for evaluating the correlation parameter g, eq 3 was changed to apply to pure polar liquids in the following form:

$$\frac{(\epsilon - n^2)}{(2\epsilon + n^2)} = \frac{1}{\epsilon_0}\,\frac{\epsilon(n^2 + 2)^2}{3(2\epsilon + n^2)^2}\,\frac{4\pi n_i' g\mu^2}{3kT} \tag{8}$$

The values of g at different temperatures obtained from eq 8

Table VII. Percent Average Deviations in SLS and Frohlich Equations Used in Prediction of Mixture Dielectric Constants

	% av dev[a]							
	SLS eq				Frohlich eq			
system	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
n-hexane (1) + toluene (2)	0.64	0.64	0.77	0.99	0.60	0.62	0.73	0.93
n-hexane (1) + chlorobenzene (2)	9.5	9.1	8.9	8.8	4.9	4.9	5.2	5.5
n-hexane (1) + 1-hexanol (2)	5.1	7.4	8.9	11	34	28	24	21

[a] Percent average deviation, given by $[\Sigma d_i^2/n]^{1/2}$ where $d = 100[(\epsilon_{\text{exptl}} - \epsilon_{\text{calcd}})/\epsilon_{\text{exptl}}]$ and n is the number of observations.

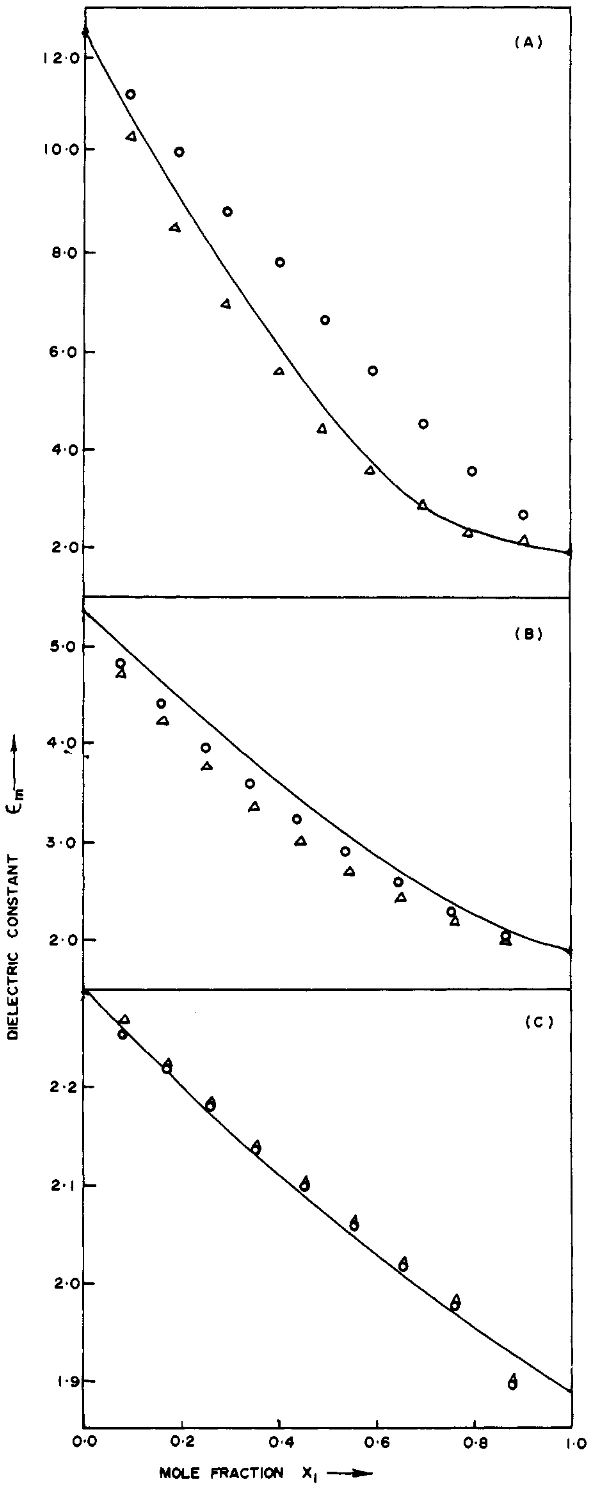

Figure 1. Plots of mixture dielectric constant vs. mole fraction for the binary systems (A) *n*-hexane (1) + 1-hexanol (2), (B) *n*-hexane (1) + chlorobenzene (2), and (C) *n*-hexane (1) + toluene (2) at 30 °C: (—) present work; (○) Frohlich equation; (△) SLS equation.

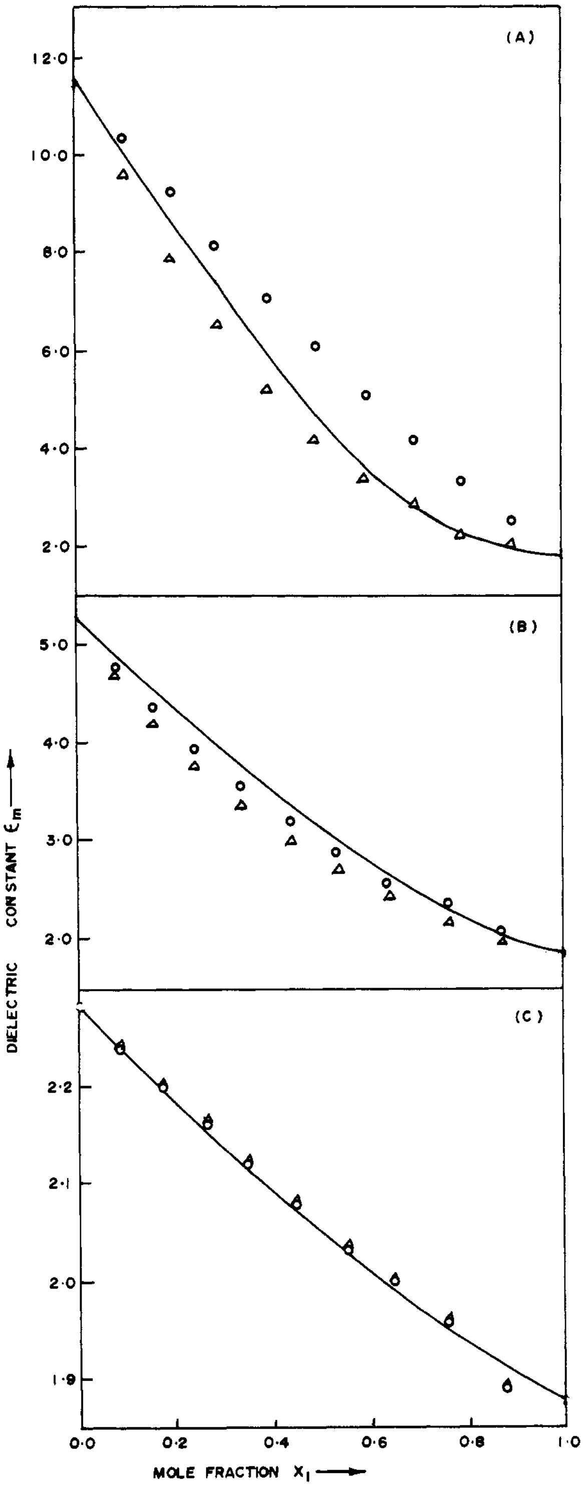

Figure 2. Plots of mixture dielectric constant vs. mole fraction for the binary systems (A) *n*-hexane (1) + 1-hexanol (2), (B) *n*-hexane (1) + chlorobenzene (2), and (C) *n*-hexane (1) + toluene (2) at 40 °C: (—) present work; (○) Frohlich equation; (△) SLS equation.

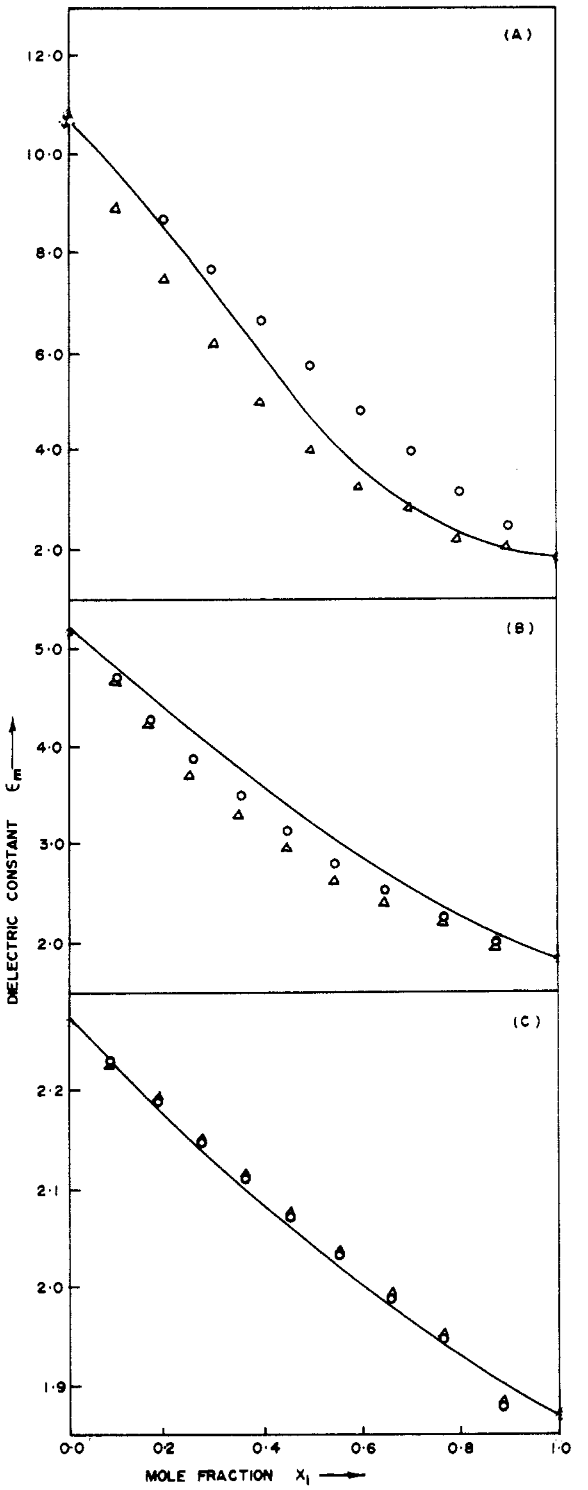

Figure 3. Plots of mixture dielectric constant vs. mole fraction for the binary systems (A) *n*-hexane (1) + 1-hexanol (2), (B) *n*-hexane (1) + chlorobenzene (2), and (C) *n*-hexane (1) + toluene (2) at 50 °C: (—) present work; (O) Frohlich equation; (Δ) SLS equation.

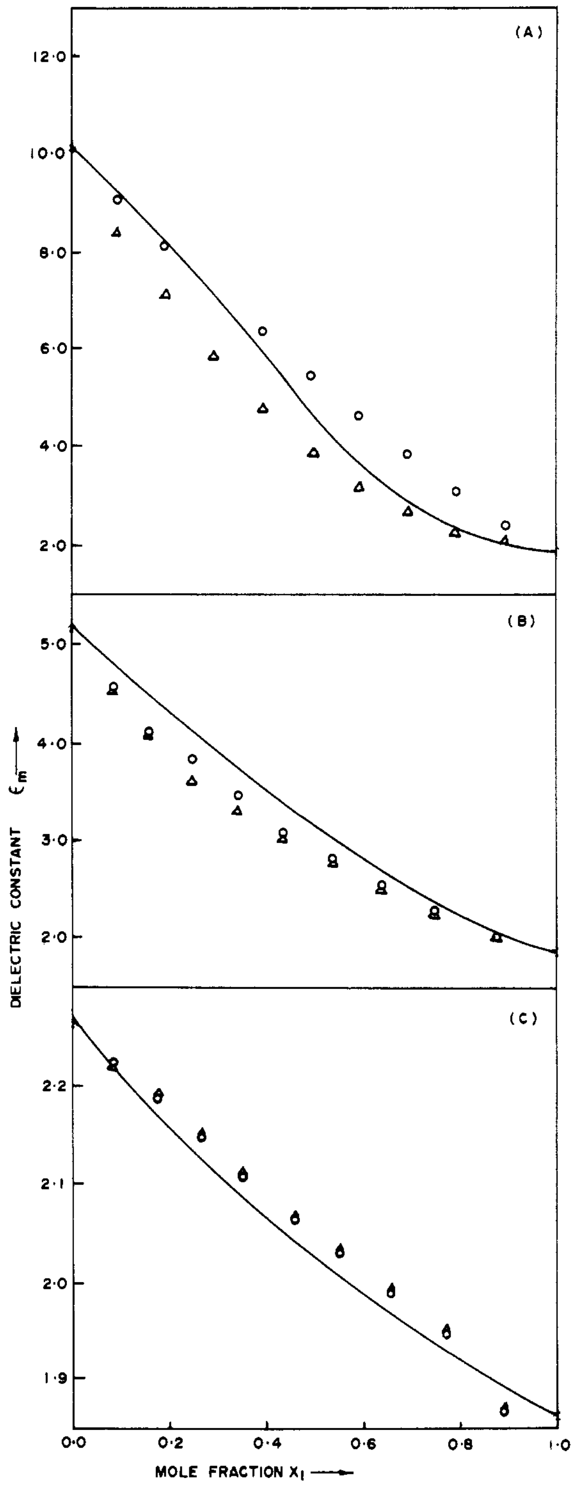

Figure 4. Plots of mixture dielectric constant vs. mole fraction for the binary systems (A) *n*-hexane (1) + 1-hexanol (2), (B) *n*-hexane (1) + chlorobenzene (2), and (C) *n*-hexane (1) + toluene (2) at 60 °C: (—) present work; (O) Frohlich equation; (Δ) SLS equation.

using required values of ϵ, n, V, and μ from Table V are included in Table VI.

Using the values of pure-component properties from Table V and the relevant values of g from Table VI, we calculated ϵ_m values from eq 5–7 for different compositions and temperatures of the binary systems studied and plotted them against binary compositions (Figures 1–4). The percent average deviations were less than ±1.0 and ±5.5 for *n*-hexane (1)–toluene (2) and *n*-hexane (1)–chlorobenzene (2), respectively, but the same was as high as ±34 for *n*-hexane (1)–1-hexanol (2) in the temperature range studied.

In view of the high percent average deviations for *n*-hexane (1)–1-hexanol (2), the dielectric constants for the binaries studied were calculated by eq 9 based on the significant liquid structure theory (*11*). Here V_s is the molar volume of a substance just before melting and V is the molar volume at the temperature of investigation. The subscript m stands for mixture properties and G is the correlation parameter. All other terms have been defined earlier in the text. For each pure liquid, the value of V_s was obtained by the method of Singh and Sinha (*12*) and that of G at each temperature was calculated by using an equation which was obtained by putting $X_2 = 0$ and

$$\frac{3\epsilon_m(\epsilon_m - n_m^2)}{(2\epsilon_m + n_m^2)} = \frac{4\pi N}{(X_1V_1 + X_2V_2)}\left[\frac{\epsilon_m(n_m^2 + 2)}{(2\epsilon_m + n_m^2)}\right]^2\left[\frac{X_1V_{s_1} + X_2V_{s_2}}{X_1V_1 + X_2V_2} \times \left(X_1^2\frac{\mu_1^2G_1}{kT} + X_2^2\frac{\mu_2^2G_2}{kT} + 2X_1X_2\frac{\mu_1\mu_2}{kT}(G_1G_2)^{1/2}\right) + \left(1 - \frac{X_1V_{s_1} + X_2V_{s_2}}{X_1V_1 + X_2V_2}\right)\left(X_1\frac{\mu_1^2}{3kT} + X_2\frac{\mu_2^2}{3kT}\right)\right] \quad (9)$$

dropping the subscripts in eq 9. The values of V_s and G so determined and included in Tables V and VI, respectively, were used to calculate ϵ_m from eq 9 for different compositions and temperatures of the binaries studied. The values of ϵ_m so calculated are plotted against binary compositions (Figures 1–4). The maximum percent average deviation for n-hexane (1)–toluene (2), n-hexane (1)–chlorobenzene (2), and n-hexane (1)–1-hexanol (2) are ±0.99, ±9.5, and ±10.5, respectively.

An inspection of the Frohlich equation (eq 5) and the SLS equation (eq 9) reveals that each one contains one adjustable parameter per component and requires only pure-component data to calculate ϵ_m. Further, from Figures 1–4, it is obvious that the experimental ϵ_m–X curves show negative nonideality and the corresponding calculated curves from eq 5 and 9 predict the same in each case. However, Table VII and Figures 1–4 reveal that the percent average deviation for eq 9 is comparable to that for eq 5 in the case of n-hexane (1)–toluene (2), somewhat higher in the case of n-hexane (1)–chlorobenzene (2), but much smaller in the case of n-hexane (1)–1-hexanol (2). Further, eq 9 gives less variation in percent average deviation at higher temperature in comparison to the same corresponding percent average deviation obtained from eq 5 in each case. Thus, it appears that eq 9, which bifurcates the mixture properties in terms of the contribution of solidlike and gaslike degrees of freedom, probably approaches reality to a better approximation for the systems studied.

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Glossary

a_i	radius of the ith type of molecule (eq 1)
g	Frohlich correlation parameter (eq 8)
k	Boltzmann constant
n	refractive index
n_i'	number of molecules per unit volume of the mixture for component i (eq 4)
G	SLS correlation parameter (eq 9)
M	molecular weight
N_i	molecules per unit volume of type i (eq 2)
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

Greek Letters

α	polarizability
ϵ	dielectric constant
ϵ_0	permittivity of free space
ϕ_i	volume fraction of the ith species under the condition $\sum\phi_i = 1$
μ	dipole moment of the free molecule, D

Subscripts

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

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