Density, Refractive Index, Viscosity, and Speed of Sound in Binary Mixtures of Ethenylbenzene with Hexane, Heptane, Octane, Nonane, Decane, and Dodecane

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Experimental densities, refractive indices, and viscosities at 298.15, 303.15, and 308.15 K and speeds of sound values at 298.15 K are presented for the binary mixtures of ethenylbenzene with hexane, heptane, octane, nonane, decane, and dodecane over the entire compositions. From these data, excess molar volumes, deviations in refractive index, speed of sound, and viscosity have been computed. These parameters have been fitted to the Redlich−Kister equation using a multiparametric nonlinear regression analysis. Estimated coefficients and standard error values for the mixing quantities are presented for each of the binary mixtures. Experimental and computed results are discussed in terms of molecular interactions.

Introduction

Ethenylbenzene (styrene) is a monomer in the preparation of an important engineering polymer, namely, polystyrene. In many processing operations, polystyrene comes in contact with organic liquids including alkanes. A literature search indicated the availability of only a few thermodynamic properties on the binary mixtures of ethenylbenzene with nitriles (Haijun et al., 1994a,b, 1995a), *N*,*N*-dimethylacetamide (Haijun et al., 1995b), *N*,*N*-dimethylformamide (Haijun et al., 1995c), and nitrobenzene (Miller et al., 1975). To our best knowledge, mixtures of ethenylbenzene with alkanes have not been studied. In view of this, we have undertaken the study of the thermodynamic, hydrodynamic, ultrasonic, and optical properties of ethenylbenzene with linear alkanes in order to understand their mixing nature. Such a study would be helpful in polymer engineering and other processing technologies.

This paper presents the physical property data on density, ρ, refractive index, n_D, for the sodium-D line, and viscosity, η, in the binary mixtures of ethenylbenzene with hexane, heptane, octane, nonane, decane, and dodecane at 298.15, 303.15, and 308.15 K, while the speeds of sound, u, are presented only at 298.15 K. From these data, excess molar volume, V^E, deviations in molar refraction, ΔR, deviations in viscosity, $\Delta \ln \eta$, and deviations in speed of sound, Δu, have been calculated, and these results are fitted to the Ridlich−Kister (1948) equation to estimate the binary coefficients and standard errors. Furthermore, these results are used to study the type and nature of intermolecular interactions between mixing components.

Experimental Section

Materials. High-purity spectroscopic and HPLC grade samples of ethenylbenzene, hexane, heptane, octane, nonane, decane, and dodecane were purchased from s.d. fine Chemicals Ltd., Mumbai, India. The GLC analyses were done on a gas chromatograph, Nucon series 5700/5765 using a flame ionization detector with fused silica columns, having a sensitivity better than 10^{-8} g of fatty acid/μL of solvent. The mol % GLC purity data of 99.6, 99.4, 99.5, 99.6, 99.7, 99.4, and 99.5 were shown respectively for ethenylbenzene, hexane, heptane, octane, nonane, decane, and dodecane. All the samples were therefore used without further purification. Experimental values of ρ and n_D of the pure liquids are compared in Table 1 at 298.15 K with the literature findings.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with Literature Values at 298.15 K

liquid (mol % purity)	$10^{-3}\ \rho$/(kg·m^{-3}) expt	lit.	n_D expt	lit.	ref
ethenylbenzene >99.7%	0.9016	0.901 51[a]	1.5440	1.544 00[b]	Haijun et al., 1995a Riddick et al., 1986
hexane (>99.6)	0.6547	0.654 89	1.3729	1.372 26	Marsh, 1995
heptane (>99.8)	0.6794	0.679 50	1.3862	1.385 13	Marsh, 1995
octane (>99.6)	0.6986	0.698 54	1.3959	1.395 12	Marsh, 1995
nonane (>99.4)	0.7141	0.713 75	1.4041	1.403 11	Marsh, 1995
decane (>99.8)	0.7264	0.726 35	1.4099	1.409 67	Marsh 1995
dodecane (>99.6)	0.7453	0.745 20	1.4278	1.427 80	Riddick et al 1986

[a] Haijun et al., 1995a. [b] Riddick et al., 1986.

Measurements. Densities of liquids and their mixtures were measured using a pycnometer having a bulb volume of 15 cm^3 and a capillary bore with an internal diameter of 1 mm. Density values are accurate to ± 0.0002 g·cm^{-3}.

Viscosities were measured using a Canon Fenske viscometer (size 75, Industrial Research Glassware, Ltd., Roselle, NJ). An electronic digital stopwatch with a readability of ± 0.01 s was used for flow time measurements. The measured viscosity values are accurate to ± 0.01 mPa·s

Refractive indices for the sodium-D line were measured using a thermostatically controlled Abbe refractometer (Bellingham and Stanley Ltd., London). A minimum of three independent readings were taken for each composition. The values of refractive indices are accurate to ± 0.0002 units.

The calibration procedures for the pycnometer, viscometer, and refractometer are the same as given earlier (Aminabhavi et al., 1993). The speeds of sound values were measured using a variable path single crystal interferometer (Mittal Enterprises, Model M-84, New Delhi) as described earlier byAralaguppi et al. (1991). The interferometer was used at a frequency of 1 kHz and was calibrated using water and benzene. The speed of sound values are accurate to ± 2 ms^{-1}.

In all the property measurements, an INSREF model 016 AP thermostat was used at a constant digital temperature display accurate to ± 0.01 K. The results of ρ, η, n_D, and u compiled in Table 2 represent the average values of three

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Table 2. Experimental Densities (ρ), Refractive Indices (n_D), Viscosity (η), and Speed of Sound (u) of the Binary Mixtures at Different Temperatures

x_1	$10^3\rho$/(kg·m^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})	x_1	$10^3\rho$/(kg·m^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})
				Ethenylbenzene (1) + Hexane (2)					
				298.15 K					
0.0000	0.6547	1.3729	0.298	1080	0.6023	0.7973	1.4737	0.457	1242
0.1019	0.6774	1.3888	0.314	1102	0.7055	0.8234	1.4919	0.507	1280
0.1987	0.6994	1.4045	0.334	1126	0.8021	0.8486	1.5086	0.566	1314
0.3024	0.7236	1.4214	0.362	1150	0.8935	0.8726	1.5247	0.632	1348
0.4003	0.7472	1.4385	0.385	1178	1.0000	0.9016	1.5440	0.709	1390
0.4992	0.7716	1.4560	0.417	1208					
				303.15 K					
0.0000	0.6501	1.3699	0.285		0.6023	0.7928	1.4715	0.436	
0.1019	0.6728	1.3862	0.302		0.7055	0.8190	1.4898	0.482	
0.1987	0.6948	1.4020	0.319		0.8021	0.8442	1.5069	0.534	
0.3024	0.7191	1.4189	0.346		0.8935	0.8682	1.5224	0.597	
0.4003	0.7426	1.4359	0.367		1.0000	0.8971	1.5415	0.662	
0.4992	0.7670	1.4536	0.397						
				308.15 K					
0.0000	0.6454	1.3672	0.273		0.6023	0.7882	1.4693	0.412	
0.1019	0.6682	1.3837	0.290		0.7055	0.8145	1.4876	0.455	
0.1987	0.6902	1.3995	0.305		0.8021	0.8397	1.5052	0.505	
0.3024	0.7145	1.4165	0.328		0.8935	0.8638	1.5201	0.560	
0.4003	0.7380	1.4333	0.351		1.0000	0.8926	1.5385	0.623	
0.4992	0.7624	1.4513	0.379						
				Ethenylbenzene (1) + Heptane (2)					
				298.15 K					
0.0000	0.6794	1.3862	0.388	1133	0.5997	0.7996	1.4713	0.500	1252
0.1018	0.6974	1.3989	0.398	1146	0.6992	0.8232	1.4881	0.536	1280
0.2020	0.7160	1.4121	0.412	1164	0.8006	0.8485	1.5060	0.581	1314
0.2988	0.7349	1.4253	0.427	1180	0.8979	0.8737	1.5241	0.638	1350
0.3984	0.7553	1.4396	0.448	1200	1.0000	0.9016	1.5440	0.709	1390
0.4989	0.7769	1.4551	0.471	1225					
				303.15 K					
0.0000	0.6751	1.3829	0.368		0.5997	0.7952	1.4684	0.473	
0.1018	0.6931	1.3963	0.379		0.6992	0.8187	1.4851	0.508	
0.2020	0.7116	1.4093	0.393		0.8006	0.8440	1.5030	0.550	
0.2988	0.7305	1.4225	0.406		0.8979	0.8694	1.5212	0.599	
0.3984	0.7509	1.4369	0.425		1.0000	0.8971	1.5415	0.662	
0.4989	0.7724	1.4523	0.445						
				308.15 K					
0.0000	0.6707	1.3812	0.349		0.5997	0.7907	1.4655	0.450	
0.1018	0.6887	1.3939	0.360		0.6992	0.8143	1.4821	0.481	
0.2020	0.7072	1.4066	0.372		0.8006	0.8396	1.5000	0.519	
0.2988	0.7261	1.4198	0.386		0.8979	0.8650	1.5184	0.565	
0.3984	0.7465	1.4341	0.405		1.0000	0.8926	1.5385	0.623	
0.4989	0.7680	1.4495	0.423						
				Ethenylbenzene (1) + Octane (2)					
				298.15 K					
0.0000	0.6986	1.3959	0.509	1180	0.5989	0.8021	1.4709	0.558	1278
0.1009	0.7132	1.4065	0.512	1192	0.7005	0.8245	1.4871	0.587	1304
0.1995	0.7286	1.4174	0.514	1204	0.8009	0.8484	1.5047	0.616	1334
0.3310	0.7505	1.4333	0.516	1222	0.8988	0.8736	1.5231	0.657	1360
0.3985	0.7626	1.4421	0.522	1234	1.0000	0.9016	1.5440	0.709	1390
0.4971	0.7813	1.4556	0.535	1254					
				303.15 K					
0.0000	0.6945	1.3935	0.478		0.5989	0.7977	1.4683	0.524	
0.1009	0.7091	1.4041	0.481		0.7005	0.8201	1.4845	0.552	
0.1995	0.7244	1.4151	0.485		0.8009	0.8440	1.5019	0.575	
0.3310	0.7463	1.4309	0.488		0.8988	0.8690	1.5203	0.617	
0.3985	0.7583	1.4397	0.495		1.0000	0.8971	1.5415	0.662	
0.4971	0.7770	1.4531	0.500						
				308.15 K					
0.0000	0.6906	1.3917	0.453		0.5989	0.8156	1.4657	0.495	
0.1009	0.7050	1.4019	0.461		0.7005	0.8394	1.4819	0.521	
0.1995	0.7420	1.4128	0.462		0.8009	0.8645	1.4991	0.550	
0.3310	0.7540	1.4285	0.464		0.8988	0.8926	1.5174	0.581	
0.3985	0.7726	1.4372	0.467		1.0000	0.8926	1.5385	0.623	
0.4971	0.7933	1.4507	0.476						
				Ethenylbenzene (1) + Nonane (2)					
				298.15 K					
0.0000	0.7141	1.4041	0.659	1198	0.5967	0.8045	1.4704	0.616	1286
0.0999	0.7262	1.4125	0.638	1212	0.6984	0.8254	1.4856	0.628	1308
0.2002	0.7395	1.4224	0.626	1224	0.7933	0.8469	1.5012	0.642	1332
0.2986	0.7535	1.4327	0.618	1234	0.8971	0.8729	1.5204	0.669	1360
0.3964	0.7687	1.4440	0.613	1248	1.0000	0.9016	1.5440	0.709	1390
0.4953	0.7855	1.4563	0.614	1266					

Table 2 (Continued)

x_1	$10^3\rho$/(kg·m^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})	x_1	$10^3\rho$/(kg·m^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})
				303.15 K					
0.0000	0.7101	1.4021	0.620		0.5967	0.8002	1.4677	0.581	
0.0999	0.7222	1.4110	0.606		0.6984	0.8210	1.4830	0.593	
0.2002	0.7354	1.4200	0.588		0.7933	0.8425	1.4985	0.606	
0.2986	0.7494	1.4300	0.582		0.8971	0.8684	1.5177	0.628	
0.3964	0.7645	1.4416	0.577		1.0000	0.8971	1.5414	0.662	
0.4953	0.7814	1.4540	0.579						
				308.15 K					
0.0000	0.7062	1.3996	0.580		0.5967	0.7959	1.4651	0.547	
0.0999	0.7182	1.4079	0.564		0.6984	0.8167	1.4804	0.558	
0.2002	0.7313	1.4175	0.551		0.7933	0.8380	1.4959	0.570	
0.2986	0.7452	1.4279	0.547		0.8971	0.8640	1.5150	0.591	
0.3964	0.7604	1.4390	0.544		1.0000	0.8926	1.5385	0.623	
0.4953	0.7771	1.4512	0.544						
				Ethenylbenzene (1) + Decane (2)					
				298.15 K					
0.0000	0.7264	1.4099	0.844	1234	0.6135	0.8095	1.4727	0.688	1298
0.1007	0.7368	1.4182	0.803	1244	0.6992	0.8264	1.4856	0.680	1314
0.2052	0.7486	1.4275	0.773	1250	0.8062	0.8498	1.5032	0.677	1338
0.2991	0.7604	1.4358	0.750	1258	0.8984	0.8728	1.5213	0.693	1360
0.4114	0.7761	1.4484	0.724	1270	1.0000	0.9016	1.5440	0.709	1390
0.4959	0.7891	1.4576	0.706	1280					
				303.15 K					
0.0000	0.7225	1.4080	0.786		0.6135	0.8052	1.4701	0.646	
0.1007	0.7327	1.4156	0.749		0.6992	0.8219	1.4827	0.638	
0.2052	0.7445	1.4248	0.722		0.8062	0.8453	1.5004	0.633	
0.2991	0.7563	1.4333	0.702		0.8984	0.8683	1.5185	0.644	
0.4114	0.7719	1.4458	0.678		1.0000	0.8971	1.5414	0.662	
0.4959	0.7849	1.4550	0.663						
				308.15 K					
0.0000	0.7186	1.4053	0.733		0.6135	0.8010	1.4675	0.607	
0.1007	0.7287	1.4134	0.700		0.6992	0.8175	1.4797	0.602	
0.2052	0.7405	1.4220	0.678		0.8062	0.8409	1.4976	0.600	
0.2991	0.7522	1.4309	0.658		0.8984	0.8638	1.5157	0.611	
0.4114	0.7678	1.4432	0.638		1.0000	0.8926	1.5385	0.623	
0.4959	0.7807	1.4524	0.624						
				Ethenylbenzene (1) + Dodecane (2)					
				298.15 K					
0.0000	0.7453	1.4271	1.330	1288	0.5987	0.8103	1.4740	0.866	1310
0.0973	0.7527	1.4327	1.243	1288	0.6990	0.8277	1.4869	0.822	1326
0.2027	0.7620	1.4405	1.143	1282	0.8005	0.8482	1.5022	0.774	1344
0.2991	0.7716	1.4464	1.062	1282	0.8996	0.8720	1.5221	0.739	1364
0.4009	0.7830	1.4541	0.990	1286	1.0000	0.9016	1.5440	0.709	1390
0.5183	0.7983	1.4654	0.909	1296					
				303.15 K					
0.0000	0.7415	1.4259	1.218		0.5987	0.8062	1.4717	0.810	
0.0973	0.7488	1.4304	1.151		0.6990	0.8235	1.4845	0.769	
0.2027	0.7581	1.4381	1.051		0.8005	0.8444	1.4989	0.722	
0.2991	0.7676	1.4443	0.985		0.8996	0.8676	1.5192	0.688	
0.4009	0.7790	1.4524	0.920		1.0000	0.8971	1.5415	0.662	
0.5183	0.7942	1.4631	0.847						
				308.15 K					
0.0000	0.7378	1.4238	1.122		0.5987	0.8021	1.4694	0.760	
0.0973	0.7451	1.4282	1.059		0.6990	0.8193	1.4820	0.724	
0.2027	0.7543	1.4358	0.980		0.8005	0.8397	1.4956	0.691	
0.2991	0.7637	1.4426	0.915		0.8996	0.8632	1.5162	0.656	
0.4009	0.7751	1.4500	0.854		1.0000	0.8926	1.5385	0.623	
0.5183	0.7901	1.4607	0.791						

independent measurements for each composition of the mixture.

Results and Discussion

Excess molar volume, V^E, and deviations in Lorentz−Lorenz molar refractivity, ΔR, viscosity, $\Delta \ln \eta$, and speed of sound, Δu, of the mixtures have been calculated from the results of ρ, n_D, η, and u given in Table 2, using the following general equation (Aminabhavi et al., 1994; Aminabhavi and Bindu, 1995):

$$Y^E \text{ (or } \Delta Y) = Y_m - x_1 Y_1 - x_2 Y_2 \qquad (1)$$

where $Y^E = V^E$ and $\Delta Y = \Delta R$, Δu, and $\Delta \ln \eta$ of the mixtures, x_i is the mole fraction of the ith component in the mixture, Y_m is the respective mixture property viz., Lorentz−Lorenz molar refractivity, R, speed of sound, u, and viscosity, η, of the mixtures), and Y_i is the respective property of the pure component, i, in the mixture. To calculate ΔR and Δu, the volume fraction, φ_i is used instead of the mole fraction (Aminabhavi et al., 1994; Aminabhavi and Bindu, 1995).

Excess molar volumes of the mixtures of ethenylbenzene + alkanes (C_6 to C_{12}) at 298.15 K are presented as a function of mole fraction, x_1, of ethenylbenzene in Figure 1. For the ethenylbenzene (1) + hexane (2) mixture, the V^E values are negative and smaller than all the other mixtures. With ethenylbenzene (1) + heptane (2) mixtures,

Table 3. Estimated Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ
Ethenylbenzene (1) + Hexane (2)					
$10^{-6}V^E$/(m^3· mol^{-1})	298.15	−1.024	0.268	0.545	0.015
	303.15	−1.126	0.317	0.345	0.013
	308.15	−1.236	0.341	0.212	0.012
$10^{-6}\Delta R$/(m^3· mol^{-1})	298.15	2.025	0.099	−0.379	0.012
	303.15	2.161	0.123	−0.142	0.017
	308.15	2.298	0.335	0.123	0.021
$\Delta \ln \eta$/(mPa·s)	298.15	−0.386	−0.008	0.095	0.007
	303.15	−0.355	−0.023	0.167	0.006
	308.15	−0.348	−0.008	0.126	0.005
Δu/(m·s^{-1})	298.15	−104.5	27.2	15.4	1.083
Ethenylbenzene (1) + Heptane (2)					
$10^{-6}V^E$/(m^3· mol^{-1})	298.15	−0.069	0.462	−0.128	0.004
	303.15	−0.115	0.508	−0.263	0.008
	308.15	−0.161	0.528	−0.305	0.011
10−6ΔR/(m3· mol−1)	298.15	0.955	−0.105	0.012	0.007
	303.15	0.982	−0.381	0.151	0.015
	308.15	0.835	−0.164	−0.107	0.010
$\Delta \ln \eta$/(mPa·s)	298.15	−0.425	0.084	−0.009	0.002
	303.15	−0.404	0.068	0.050	0.002
	308.15	−0.381	0.078	0.010	0.002
Δu/(m·s^{-1})	298.15	−146.4	22.7	2.3	0.909
Ethenylbenzene (1) + Octane (2)					
$10^{-6}V^E$/(m^3· mol^{-1})	298.15	0.546	0.235	−0.273	0.006
	303.15	0.568	0.225	−0.299	0.005
	308.15	0.680	0.270	−0.132	0.008
$10^{-6}\Delta R$/(m^3· mol^{-1})	298.15	−0.586	0.097	−0.085	0.003
	303.15	−0.598	0.010	−0.161	0.005
	308.15	−0.620	0.082	−0.321	0.003
$\Delta \ln \eta$/(mPa·s)	298.15	−0.449	0.062	0.123	0.005
	303.15	−0.431	0.078	0.136	0.007
	308.15	−0.427	0.097	0.254	0.004
Δu/(m·s^{-1})	298.15	−114.6	60.4	21.1	1.136
Ethenylbenzene (1) + Nonane (2)					
$10^{-6}V^E$/(m^3· mol^{-1})	298.15	0.814	0.216	−0.266	0.005
	303.15	0.818	0.207	−0.215	0.006
	308.15	0.913	0.279	−0.076	0.005
$10^{-6}\Delta R$/(m^3· mol^{-1})	298.15	−3.092	0.294	−0.972	0.010
	303.15	−3.185	0.330	−0.995	0.019
	308.15	−3.121	0.342	−0.962	0.009
$\Delta \ln \eta$/(mPa·s)	298.15	−0.424	0.107	−0.076	0.006
	303.15	−0.413	0.057	−0.011	0.003
	308.15	−0.396	0.052	−0.079	0.002
Δu/(m·s^{-1})	298.15	−109.3	31.6	30.2	1.454
Ethenylbenzene (1) + Decane (2)					
$10^{-6}V^E$/(m^3· mol^{-1})	298.15	1.245	0.294	−0.036	0.007
	303.15	1.314	0.323	0.148	0.008
	308.15	1.377	0.289	0.322	0.013
$10^{-6}\Delta R$/(m^3· mol^{-1})	298.15	−5.996	1.117	0.078	0.025
	303.15	−6.108	1.271	−0.449	0.025
	308.15	−6.063	1.167	−0.171	0.023
$\Delta \ln \eta$/(mPa·s)	298.15	−0.369	0.136	−0.088	0.004
	303.15	−0.339	0.144	−0.135	0.003
	308.15	−0.329	0.130	−0.070	0.004
Δu/(m·s^{-1})	298.15	−126.3	30.2	20.2	1.157
Ethenylbenzene (1) + Dodecane(2)					
$10^{-6}V^E$/(m^3· mol^{-1})	298.15	1.712	0.024	0.348	0.013
	303.15	1.760	0.215	0.243	0.034
	308.15	1.835	0.065	0.420	0.018
$10^{-6}\Delta R$/(m^3· mol^{-1})	298.15	−14.909	5.001	−0.231	0.048
	303.15	−15.122	4.995	−1.127	0.060
	308.15	−15.116	4.903	−1.453	0.070
$\Delta \ln \eta$/(mPa·s)	298.15	−0.204	0.069	0.067	0.003
	303.15	−0.171	0.072	0.054	0.006
	308.15	−0.427	0.097	0.254	0.004
Δu/(m·s^{-1})	298.15	−148.7	113.6	−55.95	2.403

the V^E results show a sigmoidal *S*-shaped composition dependence, showing a small positive part in the region rich in heptane ($x_1 < 0.4$). Such a behavior was also observed earlier by Lainez et al. (1992) for mixtures of pyridine and heptane at 298.15 K. The reasons for such an *S*-shaped behavior were given earlier by Costas and Patterson (1982), and this was attributed to the equation of state effects. All the other systems show positive V^E only. With increasing length of alkanes in the binary mixtures, the V^E increases systematically from ∼0.15 cm^3·mol^{-1} for ethenylbenzene + octane to about 0.42 cm^3·mol^{-1} for ethenylbenzene + dodecane.

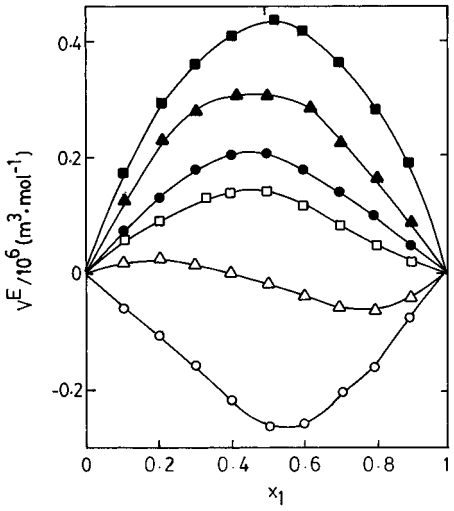

Figure 1. Dependence of excess molar volume on mole fraction of ethenylbenzene with (○) hexane, (△) heptane, (□) octane, (●) nonane, (▲) decane, and (■) dodecane at 298.15 K.

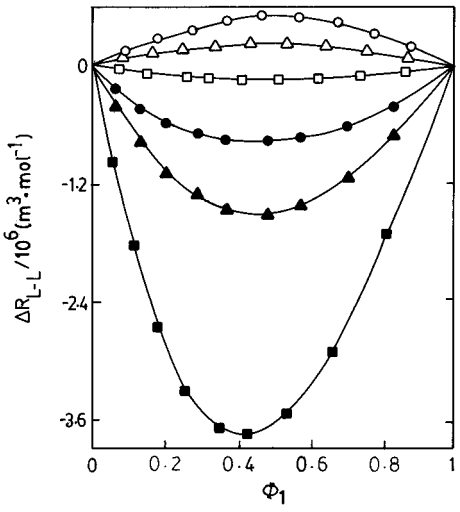

Figure 2. Dependence of deviation in molar refractivity on volume fraction of ethenylbenzene at 298.15K. Symbols are the same as given in Figure 1.

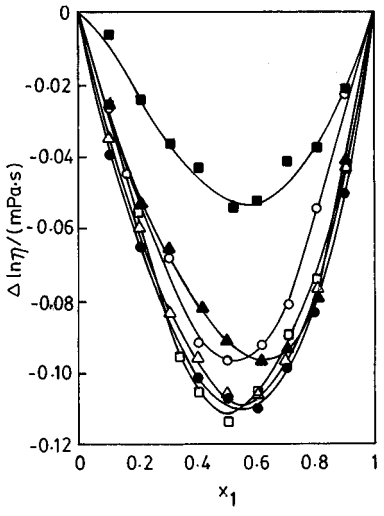

Figure 3. Dependence of deviation in ln η on mole fraction of ethenylbenzene at 298.15K. Symbols are the same as given in Figure 1.

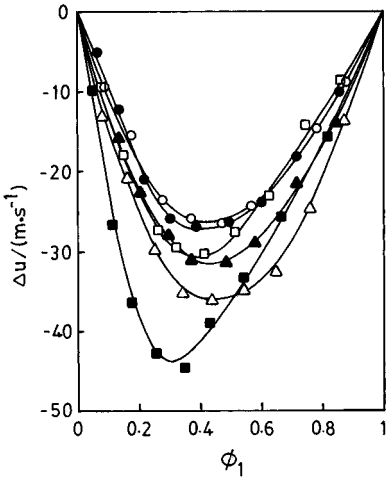

Figure 4. Dependence of deviation in speed of sound on volume fraction of ethenylbenzene at 298.15 K. Symbols are the same as given in Figure 1.

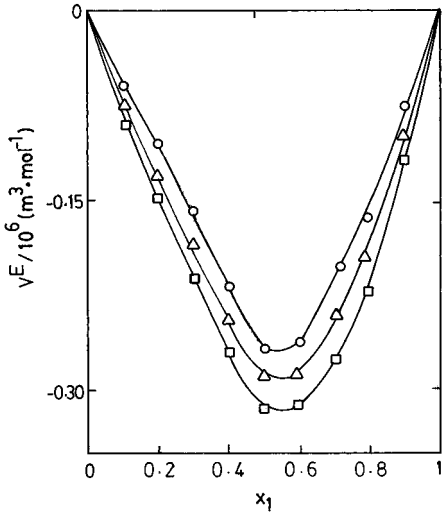

Figure 5. Dependence of excess molar volume on mole fraction for mixtures of ethenylbenzene (1) + hexane (2) at (○) 298.15 K, (△) 303.15 K, and (□) 308.15 K.

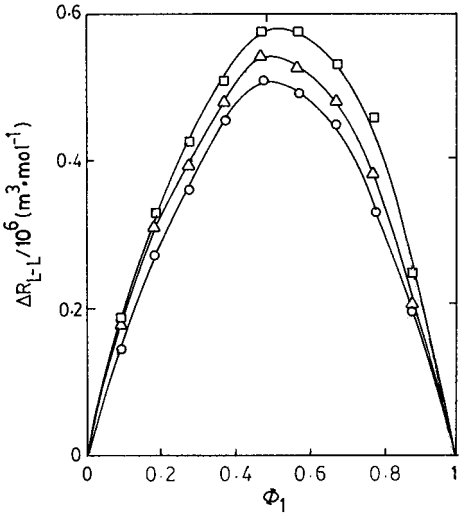

Figure 6. Dependence of deviation in molar refractivity on volume fraction for the same mixtures and temperatures as given in Figure 5.

The deviations in molar refraction, ΔR, of the mixtures at 298.15 K as calculated from the Lorentz−Lorenz equation are displayed graphically in Figure 2. For mixtures

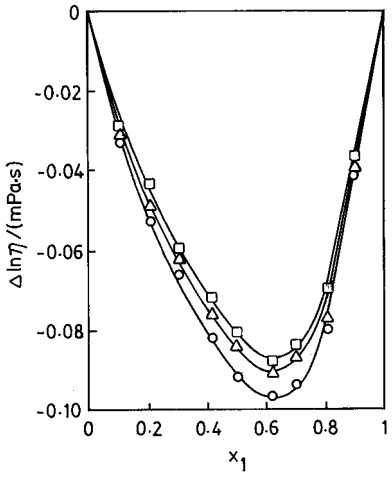

Figure 7. Dependence of deviation in ln η on mole fraction for mixtures of ethenylbenzene (1) + decane (2) at the temperatures given in Figure 5.

of ethenylbenzene + hexane, or + heptane, the ΔR values are positive, while for the remaining mixtures, the ΔR values are negative, thereby showing a decrease in ΔR with increasing size of alkanes.

The dependence of $\Delta \ln \eta$ on mole fraction x_1 at 298.15 K is displayed in Figure 3. For all the mixtures, $\Delta \ln \eta$ values are negative and do not show any systematic dependence on the size of alkanes. The results of Δu versus φ_1 are presented in Figure 4 and these values are also negative and show no systematic dependence on the size of alkanes in the mixtures.

While the calculated values of V^E, ΔR, and $\Delta \ln \eta$ show a dependence on temperature, these plots for all the liquids are not presented in order to avoid any overcrowding of the number of graphical presentations. The dependence of V^E and ΔR on temperature for mixtures of ethenylbenzene with hexane are shown in Figures 5 and 6, while the dependence of $\Delta \ln \eta$ on temperature is shown in Figure 7 for the ethenylbenzene + decane mixture. The effect of temperature on these quantities is very systematic. However, such values are not very systematic for other higher alkane-containing mixtures. It may be noted that in view of the poor solubility of tetradecane and other higher alkanes with ethenylbenzene, the properties for these mixtures are not measured.

The results of Y^E and ΔY calculated from eq 1 have been fitted to the Redlich−Kister equation (1948) to estimate the coefficients, A_i, by the method of least squares.

$$Y^E \text{ (or } \Delta Y) = x_1 x_2 \sum_{i=1}^{2} A_i (x_2 - x_1)^{i-1} \qquad (2)$$

The coefficients, A_i, along with the standard errors, σ, were calculated from

$$\sigma = [\sum_{i=1}^{n} (Y_{obs} - Y_{cal})^2/(m - p)]^{1/2} \qquad (3)$$

where Y_{obs} and Y_{cal} are the observed and calculated quantities as defined earlier, m is the number of data points, and p is the number of estimated parameters. The estimated values of A_i and σ for all the mixtures are presented in Table 3. The smoothed curves in Figures 1−7 are drawn from the fitted values, but the points in all these graphs represent the experimentally calculated values.

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