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Thermodynamic Interactions in Binary Mixtures of Ethenylbenzene with Methanol, Ethanol, Butan-1-ol, Pentan-1-ol, and Hexan-1-ol in the Temperature Range 298.15−308.15 K

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Experimental densities, viscosities, and refractive indices at 298.15, 303.15, and 308.15 K as well as the speed of sound at 298.15 K are presented over the entire mole fraction range for the binary mixtures of ethenylbenzene (styrene) with methanol, ethanol, butan-1-ol, pentan-1-ol, and hexan-1-ol. The calculated excess molar volume data have been compared with the Flory as well as the Prigogine−Flory−Patterson (PFP) theories. The deviations in logarithmic viscosity have been compared with the computed values of the Bloomfield and Dewan equation. Refractive index data have been used to calculate the deviations in the Lorentz−Lorenz molar refractivity. From the speed of sound data, the isentropic compressibility and isothermal compressibility have been calculated and compared respectively with the values computed by Benson−Kiyohara and the values from the Flory equation. All the computed quantities have been fitted to the Redlich and Kister equation to estimate the regression coefficients and standard errors. The sign and magnitude of the mixing quantities have been discussed in terms of the intermolecular interactions between ethenylbenzene and *n*-alkanols.

Introduction

Accurate experimental data on density, ρ, viscosity, η, refractive index with the sodium D-line, n_D, and speed of sound, u, of organic liquids and their binary mixtures are needed in many engineering disciplines. There has been a continued interest in the literature to test these data using the theoretical equations proposed by Flory (1965), Abe and Flory (1965), Patterson and Delmas (1970), and Patterson (1976). From a search of the literature, we find that almost no data are available on the physical property data on the binary mixtures of ethenylbenzene (styrene) with *n*-alkanols, even though several other mixtures containing styrene have been studied earlier (Aminabhavi and Patil, 1997; Haijun et al., 1994a,b, 1995a−c; Miller et al., 1975). This prompted us to present the experimental data on ρ, η, and n_D for the binary mixtures of styrene with methanol, ethanol, butan-1-o1, pentan-1-ol, and hexan-1-o1 at (298.15, 303.15, and 308.15) K over the entire mole fraction range of the mixtures. However, the results for u are reported at 298.15 K.

From density measurements, the excess molar volume V^E has been calculated and compared with the theoretically calculated V^E values obtained from the Flory theory (Flory, 1965; Abe and Flory, 1965) as well as the Prigogine−Flory−Patterson (PFP) theory (Patterson,1976; Patterson and Delmas, 1970). Viscosity data have been used to compute the deviations in logarithmic viscosity $\Delta \ln \eta$, and these are compared with the $\Delta \ln \eta$ values calculated from the Bloomfield and Dewan equation (1971). Using the refractive index data, the deviations in the Lorentz−Lorenz molar refractivity ΔR have been computed. The results of u have been used to compute the deviation in the speed of sound Δu, the deviation in the isentropic compressibility Δk_S, and the deviation in the isothermal compressibility Δk_T. The values of Δk_S also have been calculated from the Benson and Kiyohara (1979) equation. The Δk_T values have been calculated from the Flory theory (Flory, 1965; Abe and Flory, 1965). All the excess quantities have been fitted to the Redlich and Kister equation (1948) to estimate the regression coefficients and the standard errors between the experimentally calculated and fitted quantities. The sign and magnitude of these deviations have been used to study the type of thermodynamic interactions between the mixture components.

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

liquid (mol % purity)	ρ/g·cm^{-3} expt	ρ/g·cm^{-3} lit.	n_D expt	n_D lit.
styrene (99.7)	0.9016	0.9015[e]	1.5440	1.5440[d]
methanol (99.6)	0.7866	0.7866[a]	1.3273	1.3274[c]
ethanol (99.8)	0.7855	0.7850[a]	1.3603	1.3594[d]
propan-1-ol (99.6)	0.7998	0.7996[d]	1.3835	1.3833[c]
butan-1-ol (99.4)	0.8059	0.8058[d]	1.3974	1.3974[c]
pentan-1-ol (99.8)	0.8110	0.8109[b]	1.4085	1.4080[d]
hexan-1-ol (99.6)	0.8153	0.8153[d]	1.4164	1.4160[c]

[a] Won et al., 1981. [b] Ortega et al., 1982. [c] Ortega et al., 1986. [d] Riddick et al., 1986. [e] Haijun et al., 1995.

Materials and Methods

Materials. High-purity spectroscopic and HPLC grade samples of ethenylbenzene, methanol, propan-1-ol, and butan-1-ol were purchased from s.d. fine Chemicals Ltd., Mumbai, India. Ethanol was purchased from E. Merk. Pentan-1-ol and hexan-1-ol were obtained from Fluka. Their GLC analyses indicated a mole percent purity of >99%. These analyses were performed on a HP 6890 series gas chromotagraph, using a flame ionization detector with fused silica columns. All the samples were used without further purification. Experimental values of ρ and n_D of

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

x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})	x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})	x_1	ρ/(g·cm^{-3})	n_D	η/(mPa·s)	u/(m·s^{-1})
		styrene + methanol					styrene + propan-1-ol					styrene + pentan-1-ol (2)		
		298.15 K					298.15 K					298.15 K		
0.0000	0.7866	1.3273	0.538	1118	0.0000	0.7998	1.3835	1.927	1216	0.0000	0.8110	1.4085	3.421	1280
0.1005	0.8167	1.3807	0.591	1170	0.0999	0.8157	1.4067	1.594	1238	0.1003	0.8209	1.4220	2.791	1288
0.1920	0.8362	1.4184	0.623	1208	0.1997	0.8296	1.4287	1.326	1262	0.1994	0.8305	1.4351	2.141	1296
0.3007	0.8534	1.4473	0.650	1250	0.2980	0.8418	1.4464	1.153	1284	0.3003	0.8400	1.4489	1.602	1305
0.4018	0.8653	1.4707	0.669	1284	0.3952	0.8524	1.4652	1.011	1302	0.3977	0.8489	1.4620	1.320	1314
0.4981	0.8746	1.4902	0.679	1308	0.4985	0.8627	1.4806	0.892	1320	0.4969	0.8579	1.4753	1.112	1324
0.5994	0.8824	1.5045	0.686	1324	0.6022	0.8721	1.4963	0.815	1336	0.5963	0.8662	1.4886	0.984	1336
0.7011	0.8889	1.5119	0.692	1342	0.6984	0.8802	1.5119	0.762	1348	0.7027	0.8760	1.5027	0.859	1349
0.8049	0.8944	1.5280	0.701	1356	0.7985	0.8879	1.5219	0.727	1362	0.8026	0.8847	1.5162	0.783	1362
0.8981	0.8985	1.5357	0.706	1372	0.9019	0.8952	1.5317	0.707	1376	0.9011	0.8932	1.5296	0.737	1376
1.0000	0.9016	1.5440	0.709	1390	1.0000	0.9016	1.5440	0.709	1390	1.0000	0.9016	1.5440	0.709	1390
		303.15 K					303.15 K					303.15 K		
0.0000	0.7817	1.3256	0.503		0.0000	0.7817	1.3756	0.503		0.0000	0.8074	1.4070	3.007	
0.1005	0.8118	1.3786	0.550		0.0999	0.8118	1.3786	0.550		0.1003	0.8171	1.4199	2.472	
0.1920	0.8313	1.4165	0.583		0.1997	0.8313	1.4165	0.583		0.1994	0.8266	1.4327	1.984	
0.3007	0.8484	1.4430	0.608		0.2980	0.8484	1.4430	0.608		0.3003	0.8359	1.4465	1.404	
0.4018	0.8606	1.4633	0.618		0.3952	0.8606	1.4633	0.618		0.3977	0.8448	1.4592	1.175	
0.4981	0.8698	1.4866	0.634		0.4985	0.8698	1.4866	0.634		0.4969	0.8536	1.4730	1.013	
0.5994	0.8777	1.4962	0.642		0.6022	0.8777	1.4962	0.642		0.5963	0.8625	1.4878	0.901	
0.7011	0.8842	1.5120	0.646		0.6984	0.8842	1.4898	0.646		0.7027	0.8717	1.4997	0.793	
0.8049	0.8897	1.5206	0.655		0.7985	0.8897	1.5206	0.655		0.8026	0.8804	1.5138	0.741	
0.8981	0.8938	1.5224	0.661		0.9019	0.8938	1.5224	0.661		0.9011	0.8887	1.5250	0.692	
1.0000	0.8971	1.5415	0.662		1.0000	0.8971	1.5415	0.662		1.0000	0.8971	1.5414	0.662	
		308.15 K					308.15 K					308.15 K		
0.0000	0.7769	1.3231	0.470		0.0000	0.7769	1.3731	0.470		0.0000	0.8037	1.4048	2.607	
0.1005	0.8068	1.3762	0.515		0.0999	0.8068	1.3762	0.515		0.1003	0.8133	1.4177	2.166	
0.1920	0.8263	1.4137	0.543		0.1997	0.8263	1.4137	0.543		0.1994	0.8227	1.4303	1.638	
0.3007	0.8436	1.4420	0.569		0.2980	0.8436	1.4420	0.569		0.3003	0.8319	1.4437	1.250	
0.4018	0.8558	1.4650	0.587		0.3952	0.8558	1.4650	0.587		0.3977	0.8407	1.4564	1.046	
0.4981	0.8651	1.4843	0.594		0.4985	0.8651	1.4843	0.594		0.4969	0.8495	1.4708	0.915	
0.5994	0.8731	1.4988	0.598		0.6022	0.8731	1.4988	0.598		0.5963	0.8582	1.4873	0.820	
0.7011	0.8796	1.5121	0.602		0.6984	0.8796	1.5121	0.602		0.7027	0.8674	1.4967	0.722	
0.8049	0.8851	1.5251	0.610		0.7985	0.8851	1.5251	0.610		0.8026	0.8760	1.5113	0.680	
0.8981	0.8892	1.5321	0.617		0.9019	0.8892	1.5321	0.617		0.9011	0.8843	1.5245	0.637	
1.0000	0.8926	1.5385	0.623		1.0000	0.8926	1.5385	0.623		1.0000	0.8926	1.5385	0.623	
		styrene (1) + ethanol (2)					styrene + butan-1-ol					styrene + hexan-1-ol		
		298.15 K					298.15 K					298.15 K		
0.0000	0.7855	1.3603	1.084	1162	0.0000	0.8056	1.3974	2.540	1248	0.0000	0.8153	1.4164	4.216	1328
0.0997	0.8081	1.3971	1.010	1196	0.0999	0.8183	1.4151	1.971	1264	0.0998	0.8234	1.4286	3.131	1330
0.1994	0.8260	1.4212	0.932	1228	0.2019	0.8299	1.4331	1.644	1282	0.2024	0.8318	1.4410	2.522	1332
0.3013	0.8413	1.4453	0.849	1258	0.2994	0.8403	1.4488	1.368	1298	0.3078	0.8406	1.4536	1.956	1336
0.3987	0.8537	1.4655	0.798	1284	0.3982	0.8503	1.4638	1.165	1314	0.4006	0.8484	1.4649	1.613	1341
0.5004	0.8645	1.4825	0.764	1304	0.5226	0.8622	1.4819	0.969	1332	0.5007	0.8570	1.4773	1.293	1348
0.6011	0.8737	1.4995	0.747	1324	0.6020	0.8694	1.4933	0.913	1342	0.5988	0.8655	1.4896	1.134	1355
0.7001	0.8819	1.5122	0.737	1340	0.7030	0.8782	1.5069	0.821	1355	0.6993	0.8743	1.5026	0.972	1364
0.7976	0.8890	1.5232	0.731	1358	0.7942	0.8858	1.5189	0.772	1366	0.7986	0.8832	1.5160	0.891	1372
0.8989	0.8957	1.5288	0.720	1374	0.8935	0.8937	1.5317	0.729	1378	0.8985	0.8923	1.5296	0.808	1380
1.0000	0.9016	1.5440	0.709	1390	1.0000	0.9016	1.5440	0.709	1390	1.0000	0.9016	1.5440	0.708	1390
		303.15 K					303.15 K					303.15 K		
0.0000	0.7811	1.3586	0.986		0.0000	0.8018	1.3955	2.324		0.0000	0.8117	1.4146	3.567	
0.0997	0.8034	1.3949	0.930		0.0999	0.8140	1.4134	1.809		0.0998	0.8197	1.4265	2.773	
0.1994	0.8214	1.4195	0.861		0.2019	0.8257	1.4312	1.470		0.2024	0.8280	1.4389	2.177	
0.3013	0.8367	1.4430	0.777		0.2994	0.8361	1.4466	1.230		0.3078	0.8366	1.4515	1.703	
0.3987	0.8490	1.4633	0.735		0.3982	0.8460	1.4616	1.052		0.4006	0.8445	1.4627	1.446	
0.5004	0.8598	1.4800	0.711		0.5226	0.8577	1.4796	0.885		0.5007	0.8529	1.4750	1.154	
0.6011	0.8691	1.4962	0.701		0.6020	0.8648	1.4910	0.830		0.5988	0.8614	1.4872	1.051	
0.7001	0.8773	1.5099	0.693		0.7030	0.8736	1.5044	0.767		0.6993	0.8701	1.5002	0.890	
0.7976	0.8845	1.5206	0.688		0.7942	0.8813	1.5162	0.721		0.7986	0.8789	1.5135	0.840	
0.8989	0.8911	1.5265	0.679		0.8935	0.8935	1.5293	0.681		0.8985	0.8879	1.5270	0.747	
1.0000	0.8971	1.5415	0.662		1.0000	1.0000	1.5414	0.662		1.0000	0.8971	1.5415	0.662	
		308.15 K					308.15 K					308.15 K		
0.0000	0.7767	1.3553	0.898		0.0000	0.7978	1.3937	1.968		0.0000	0.8081	1.4122	2.766	
0.0997	0.7987	1.3926	0.848		0.0999	0.8097	1.4119	1.636		0.0998	0.8160	1.4245	2.296	
0.1994	0.8167	1.4171	0.786		0.2019	0.8213	1.4294	1.327		0.2024	0.8243	1.4368	1.880	
0.3013	0.8320	1.4406	0.711		0.2994	0.8317	1.4445	1.104		0.3078	0.8329	1.4492	1.497	
0.3987	0.8444	1.4610	0.681		0.3982	0.8416	1.4594	0.950		0.4006	0.8405	1.4605	1.298	
0.5004	0.8550	1.4778	0.661		0.5226	0.8533	1.4774	0.811		0.5007	0.8489	1.4727	1.114	
0.6011	0.8644	1.4938	0.652		0.6020	0.8604	1.4887	0.762		0.5988	0.8572	1.4849	1.008	
0.7001	0.8726	1.5077	0.645		0.7030	0.8691	1.5017	0.693		0.6993	0.8659	1.4977	0.860	
0.7976	0.8799	1.5194	0.640		0.7942	0.8767	1.5134	0.660		0.7986	0.8746	1.5111	0.810	
0.8989	0.8865	1.5242	0.634		0.8935	0.8846	1.5270	0.630		0.8985	0.8835	1.5244	0.693	
1.0000	0.8926	1.5385	0.623		1.0000	0.8926	1.5385	0.623		1.0000	0.8926	1.5385	0.623	

Table 3. Estimated Parameters of Various Functions for the Binary Mixtures

function	temp/K	A_0	A_1	A_2	σ	function	temp/K	A_0	A_1	A_2	σ
styrene (1) + methanol (2)						styrene (1) + butan-1-ol (2)					
$V^E/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−1.096	−0.058	−0.773	0.007	$V^E/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−0.428	−0.207	−0.394	0.003
	308.15	−1.071	−0.066	−0.698	0.004		303.15	−0.389	−0.250	−0.347	0.008
	308.15	−1.054	−0.046	−0.505	0.005		308.15	−0.374	−0.211	−0.088	0.007
$\Delta R/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−26.16	−13.82	−9.30	0.119	$\Delta R/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−2.99	−0.37	0.04	0.015
	303.15	−25.73	−15.25	−15.89	0.396		303.15	−3.00	−0.41	0.16	0.016
	308.15	−26.37	−13.68	−7.14	0.039		308.15	−2.97	−0.45	−0.41	0.025
$\Delta \ln \eta/(\mathrm{mPa{\cdot}s})$	298.15	0.375	0.284	0.168	0.002	$\Delta \ln \eta/(\mathrm{mPa{\cdot}s})$	298.15	−1.12	−0.059	−0.061	0.013
$\Delta u/(\mathrm{m\ s^{-1}})$	298.15	211.0	105.1	−58.7	1.712	$\Delta u/(\mathrm{m\ s^{-1}})$	298.15	38.6	0.1	−18.6	0.452
$\Delta k_s/(\mathrm{T\ Pa^{-1}})$	298.15	−102.76	−17.89	80.86	3.402	$\Delta k_s/(\mathrm{T\ Pa^{1-}})$	298.15	−57.67	−0.52	18.66	0.384
styrene (1) + ethanol (2)						styrene (1) + pentan-1-ol (2)					
$V^E/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−0.759	−0.648	−0.339	0.006	$V^E/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−0.259	−0.271	−0.099	0.004
	303.15	−0.696	−0.594	−0.273	0.006		303.15	−0.186	−0.199	−0.082	0.006
	308.15	−0.624	−0.589	−0.224	0.007		308.15	−0.144	−0.211	−0.097	0.004
$\Delta R/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−14.87	−5.43	−1.80	0.132	$\Delta R/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−0.86	−0.19	−0.39	0.007
	303.15	−14.89	−5.47	−1.818	0.123		303.15	−0.82	−0.14	−1.32	0.057
	308.15	−14.79	−5.37	−1.20	0.121		308.15	−0.83	−0.18	−0.27	0.006
$\Delta\ln\eta/(\mathrm{mPa.s})$	298.15	−0.548	−0.095	0.416	0.006	$\Delta \ln \eta/(\mathrm{mPa{\cdot}s})$	298.15	−1.38	0.193	0.621	0.024
$\Delta u/(\mathrm{m\ s^{-1}})$	298.15	114.3	4104	−20.2	1.115	$\Delta u/(\mathrm{m\ s^{-1}})$	298.15	−41.3	1.4	10.2	0.226
$\Delta k_s/(\mathrm{TPa^{1-}})$	298.15	−90.57	8.95	48.76	0.830	$\Delta k_s/(\mathrm{T\ Pa^{1-}})$	298.15	13.74	0.74	−11.24	0.230
styrene (1) + propan-1-ol (2)						styrene (1) + hexan-1-ol (2)					
$V^E/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−0.622	−0.458	−0.351	0.007	$V^E/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−0.120	−0.028	−0.056	0.001
	303.15	−0.209	−0.438	−0.284	0.088		303.15	−0.105	−0.034	−0.012	0.006
	308.15	−0.476	−0.448	−0.190	0.008		308.15	−0.100	−0.027	−0.058	0.001
$\Delta R/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	−7.64	−1.34	−0.43	0.073	$\Delta R/10^{-6}$ ($\mathrm{m^3\ mol^{-1}}$)	298.15	0.61	−0.32	0.21	0.004
	303.15	−7.48	−1.45	−1.47	0.085		303.15	0.60	−0.37	−0.00	−0.010
	308.15	−7.51	−1.50	−2.07	0.102		308.15	0.66	−0.34	−0.30	0.006
$\Delta \ln \eta/(\mathrm{mPa{\cdot}s})$	298.15	−1.07	0.051	−0.019	0.005	$\Delta \ln \eta/(\mathrm{mPa.s})$	298.15	−1.08	−0.14	0.39	0.020
$\Delta \mathrm{u}/(\mathrm{m\ s^{-1}})$	298.15	69.4	23.2	−37.5	0.794	$\Delta u/(\mathrm{m\ s^{-1}})$	298.15	−44.93	−15.01	3.38	0.604
$\Delta k_s/(\mathrm{TPa^{1-}})$	298.15	−72.45	8.09	50.31	0.550	$\Delta k_s/(\mathrm{T\ Pa^{1-}})$	298.15	20.96	−21.78	−1.59	0.753

the pure liquids are compared in Table 1 at 298.15 K and these agree with the published results. Mixtures were prepared by mass in specially designed glass-stoppered bottles and were used on the same day. An electronic Mettler balance, model AE 240, with a precision of ±0.01 mg was used for the mass measurements. The error in mole fraction is around ±0.0002.

Methods. 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 Cannon Fenske viscometer (size 75, Industrial Research Glassware, Ltd., New Jersey). 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. The experimental details and calibrations of both the pycnometer and the viscometer are the same as those reported earlier (Aminabhavi and Bindu, 1994, 1995; Aminabhavi et al., 1993; Aralaguppi et al., 1991).

Refractive indices for the sodium D-line were measured using a thermostatically controlled Abbe refractometer (Bellingham and Stanley Ltd., England). A minimum of three independent readings were taken for each composition. The refractive index values are accurate to ±0.0002 units. Calibration of the refractometer is the same as that given earlier (Aralaguppi et al., 1991).

The speed of sound values were measured using a variable-path single-crystal interferometer (Mittal Enterprises, Model M-84, New Delhi), as described earlier (Aralaguppi 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 m·s^{-1}. From the measured speed of sound data, the values of isentropic compressibility k_s have been calculated as $k_s = 1/u^2\rho$.

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

Results

Excess Molar Volume. Excess molar volume was calculated from the experimental densities using

$$V^E = V_m - V_1 x_1 - V_2 x_2 \qquad (1)$$

where $V_m = (M_1x_1 + M_2x_2)/\rho$, $V_1 = M_1/\rho_1$, and $V_2 = M_2/\rho_2$ are respectively the molar volume of the mixture, the volume of component 1, and the volume of component 2; M_1 and M_2 are the respective molecular weights; and x_1 and x_2 are the mole fractions of the respective components.

The V^E values from the Flory equation (Flory, 1965; Abe and Flory, 1965) were calculated as

$$V^E = \left(\sum_{i=1}^{2} x_i V_i^*\right)(\tilde{V}^{\circ 7/3}/[4/3 - (\tilde{V}^\circ)^{1/3}])(\tilde{T} - \tilde{T}^\circ) \qquad (2)$$

where $\tilde{V}^\circ$ is the ideal reduced volume, V_i^* is the characteristic volume of the i-th component, $\tilde{T}$ is the reduced temperature, and $\tilde{T}^\circ$ is the ideal reduced temperature. The V^E results have also been calculated from the PFP theories (Patterson, 1976; Patterson and Delmas, 1970).

Deviation in Logarithmic Viscosity. Several empirical correlations have been proposed to study the viscosity behavior of liquid mixtures that generally require adjustable parameters (Vishwanath and Natarajan, 1989; Reid et al., 1987). However, the most commonly used equation to predict the deviation in logarithmic viscosity $\Delta \ln \eta$ is

$$\Delta \ln \eta = \ln \eta_{mix} - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \qquad (3)$$

Here, η_{mix} refers to the mixture viscosity; and η_1 and η_2

are the individual component viscosities. Bloomfield and Dewan (1971) developed a theoretical relation to compute the $\Delta \ln \eta$ term without any adjustable parameters.

Deviation in Ultrasonic Properties. Ultrasonic properties of liquids/liquid mixtures are useful in predicting the deviations in isentropic compressibility Δk_S and isothermal compressibility Δk_T using a general equation of the type (Aminabhavi and Bindu, 1994, 1995)

$$\Delta k_s \text{ (or } \Delta k_T) = \Delta k_s \text{ (or } \Delta k_T)^{\text{mix}} - \Delta k_s \text{ (or } \Delta k_T)^{\text{ideal}} \quad (4)$$

The ideal terms in eq 4 can be computed from the sums of the contributions of the individual components of the mixture. The k_s^{ideal} and k_T^{ideal} terms have been calculated using the Benson and Kiyohara (1979) procedure.

A survey of the literature indicates that very few attempts (Douheret et al., 1995) have been made to predict Δk_T theoretically. This prompted us to compute Δk_T of the mixtures using the Flory theory (Flory 1965; Abe and Flory, 1965):

$$\Delta k_T = 3\tilde{V}^2/P^*[(\tilde{V}^{1/3} - 1)^{-1} - 3] - \sum_{i=1}^{2}(\Phi_i \bar{V}_i k_{T,i})/\bar{V} \quad (5)$$

where the symbols have the same meanings as before.

Deviations in the speed of sound Δu have been calculated from the experimental values of u_{mix} for the binary mixtures and of u_i for the individual components using the relation

$$\Delta u = u_{\text{mix}} - u_1 x_1 - u_2 x_2 \quad (6)$$

Deviation in Molar Refraction. Using the experimental values of n_D, the deviations in molar refraction ΔR have been computed (Aminabhavi and Bindu, 1994, 1995) as

$$\Delta R = R_{\text{mix}} - R_1\Phi_1 - R_2\Phi_2 \quad (7)$$

Here, R_{mix} refers to molar refractivity of the mixture, and R_i is the molar refractivity of the pure component i in the mixture. The molar refractivity R_i was calculated using the well-known Lorentz–Lorenz mixing rule.

Least Squares Estimations. Experimentally calculated V^E (from eq 1), $\Delta \ln \eta$ (from eq 3), Δk_S (from eq 4), Δu (from eq 6), and ΔR (from eq 7) have been fitted to the Redlich and Kister equation (1948) to obtain the regression coefficients A_j.

$$\Delta Y = c_1 c_2 \sum_{j=1}^{k} A_j (c_2 - c_1)^{j-1}$$

where ΔY refers to V^E, $\Delta \ln \eta$, Δk_S, Δu, or ΔR, and c_i is the mixture composition (mole fraction or volume fraction, depending upon the quantity to be calculated). Following the conventional practice in the literature, the volume fraction Φ_i was used to calculate Δk_S and ΔR. However, the mole fraction x_i was used to calculate V^E, $\Delta \ln \eta$, and Δu.

The standard error values σ between the calculated and observed data points are obtained by using

$$\sigma = \sum\{(Y^E_{\text{cal}} - Y^E_{\text{obs}})^2/(n - m)\}^{1/2}$$

Values of the coefficients A_i and σ are given in Table 3. In all these calculations, not more than three coefficients were required in the polynomial for a better fit while minimizing the data points using the Marquardt algorithm (1963).

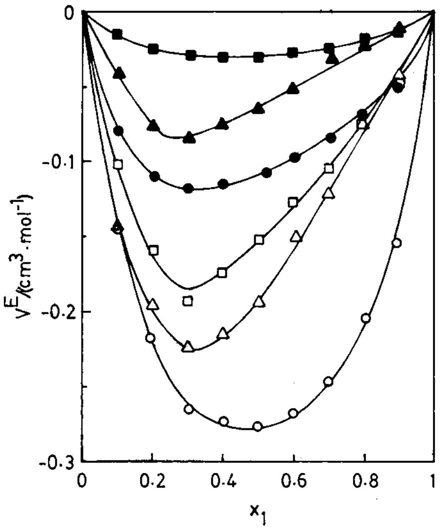

Figure 1. Excess volume versus mole fraction of styrene with (○) methanol, (△) ethanol, (□) propan-1-ol, (●) butan-1-ol, (▲) pentan-1-ol, and (■) hexan-1-ol at 298.15 K.

Discussion

The results of V^E at 298.15 K as a function of mole fraction of styrene calculated from eq 1 are displayed in Figure 1. Due to the wide differences in the molar volume and dipole moment values of styrene ($V_1 = 115.5$ cm^3·mol^{-1} and $\mu_1 = 0.43$) and that of methanol ($V_2 = 40.7$ cm^3·mol^{-1} and $\mu_2 = 2.87$), a large negative V^E is observed. This may be due to the presence of specific interactions arising from the hydrogen bond type effects between the hydroxyl group of methanol and the vinyl group of styrene. Earlier studies by Wilson et al. (1985) have shown the formation of H-bonds due to self-association in *n*-alkanols. Our V^E data support the capabilities of *n*-alkanols to break up the molecular associations, which tend to decrease with increasing size of *n*-alkanols. For instance, the V^E values of styrene + hexan-1-ol mixtures are less negative. However, due to the electron-donating inductive effect of the alkyl group, the strength of bonding in *n*-alkanols is also expected to decrease with increasing size of *n*-alkanols, thereby implying that higher *n*-alkanols have less proton donor ability. Styrene has a strongly oriented structure, which is stabilized by the dipole–dipole interactions. Note that the V^E versus x_1 curves from ethanol- to pentan-1-ol-containing mixtures are shifted slightly toward a lower composition of styrene in the mixtures, indicating higher interactions in the *n*-alkanol-rich region. The experimental V^E results are compared in Figures 2 and 3 with the calculated values of the PFP and Flory theories, respectively, in the case of styrene + methanol, + ethanol, + butan-1-ol, or + hexan-1-ol mixtures.

The plots of $\Delta \ln \eta$ versus x_1 at 298.15 K presented in Figure 4 show an opposite trend to those of the V^E results; that is, the $\Delta \ln \eta$ values decrease systematically from methanol to pentan-1-ol. Also, except for styrene + methanol, for all the other *n*-alkanol-containing mixtures, the $\Delta \ln \eta$ values are negative over the entire range of mixture composition. However, for the styrene + hexan-1-ol mixture, the $\Delta \ln \eta$ values are almost identical to those for the styrene + propan-1-ol mixture. Though the dependence of temperature on $\Delta \ln \eta$ is not very systematic for the lower *n*-alkanols (C_1 to C_2), but for the higher *n*-alkanols (C_4 to

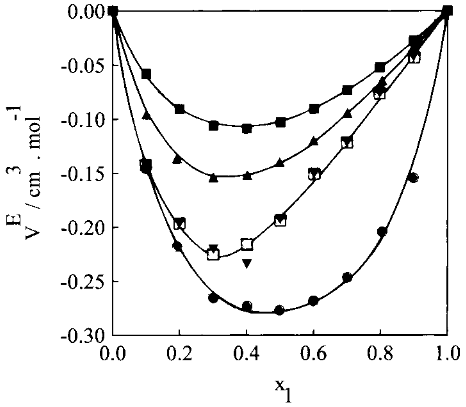

Figure 2. Comparison of V^E data for mixtures of styrene with methanol [(○) expt; (▲) Flory theory; (◆) PFP theory] and for mixtures of styrene with ethanol (□) expt; (■) Flory theory; (▼) PFP theory] at 298.15 K.

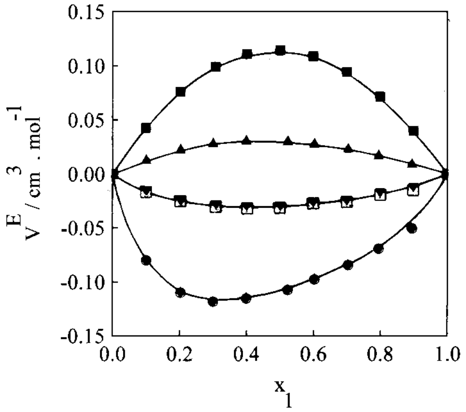

Figure 3. Comparison of V^E data for mixtures of styrene with butan-1-ol [(O) expt; (▲) Flory theory; (◆) PFP theory] and for mixtures of styrene with hexan-1-ol [(□) expt; (■) Flory theory; (▼) PFP theory] at 298.15 K.

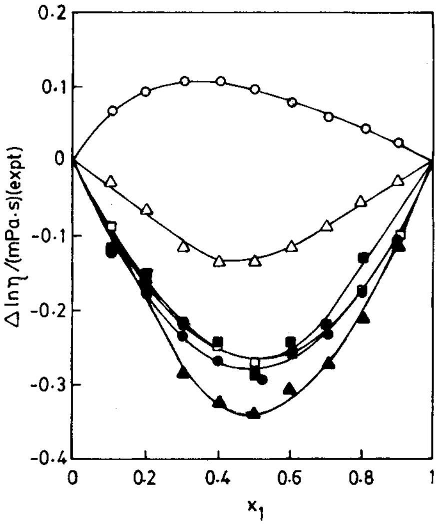

Figure 4. Deviations in ln *η* versus mole fraction of styrene with *n*-alkanols at 298.15 K. Symbols are the same as those in Figure 1.

C_6), a regular increase in Δln*η* is observed with temperature. For the mixtures of styrene + butan-1-ol, or + hexan-1-ol, the Δ ln *η* curves vary almost identically. However, mixtures of styrene + pentan-1-ol show the lowest Δ ln *η* values among the mixtures studied. The results of Δ ln *η* at 298.15 K calculated from the Bloomfield and Dewan equation (1971) are compared with the experimental data in Table 4. The theoretical Δ ln *η* values are positive in all cases. However, both the experimental and theoretical Δ ln *η* values show similar variations (Figure 4).

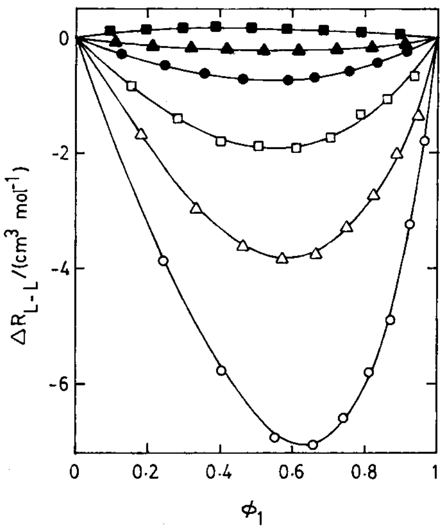

Figure 5. Excess molar refractivity versus volume fraction of styrene + *n*-alkanol mixtures at 298.15 K. Symbols are the same as those in Figure 1.

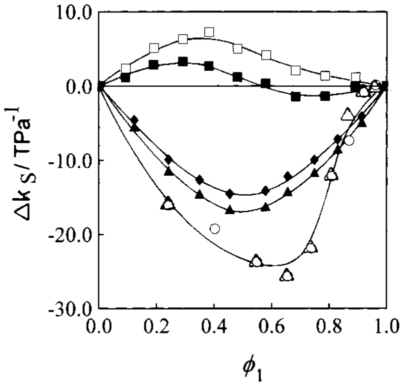

Figure 6. Comparison of experimental deviations in isentropic compressibility (Δk_S) for styrene with (○) methanol, (◆)butan-1-ol, and (□) hexan-1-ol with those calculated from Benson and Kiyohara theory at 298.15 K for mixtures of styrene with (△) methanol, (▲) butan-1-ol, and (■) hexan-1-ol.

Table 4. Comparison of Theoretical Values with the Experimentally Calculated Data at 298.15 K at Equimolar Composition for Mixtures of Styrene + *n*-Alkanol

	Δ ln *η*		$V^E/10^{-6}$ (m^{-3}·mol^{-1})		
styrene +	expt	theo	expt	PFP	flory
methanol	0.096	0.266	−0.277	−0.277	−0.140
ethanol	−0.137	0.139	−0.194	−0.194	−0.103
butan-1-ol	−0.296	0.098	−0.106	−0.107	0.031
pentan-1-ol	−0.341	0.087	−0.064	−0.063	0.111
hexan-1-ol	−0.289	0.077	−0.031	−0.030	0.114

The results of Δ*R* displayed in Figure 5 at 298.15 K show an increasing trend with the increasing size of *n*-alkanol molecules. For styrene + hexan-1-ol, the Δ*R* values are slightly positive, while, for the remaining mixtures, these are negative, showing a slight shift in the minima for styrene + methanol or + ethanol mixtures at higher compositions of styrene.

Experimentally calculated values of Δk_S are compared in Figure 6 with those calculated from the Benson and Kiyohara theory (1979) at 298.15 K for the mixtures of

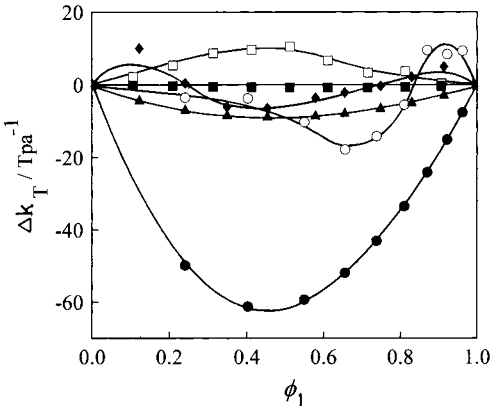

Figure 7. Comparison of experimental deviations in isothermal compressibility (Δk_T) for styrene with (○) methanol, (◆) butan-1-ol, and (□) pentan-1-ol with Flory theory for styrene with (●) methanol, (▲) butan-1-ol, and (■) pentan-1-ol at 298.15 K.

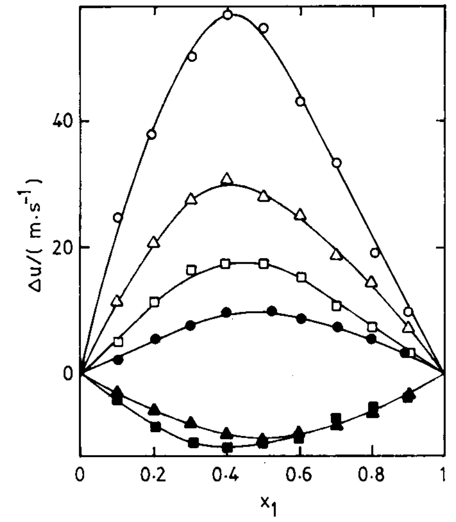

Figure 8. Deviations in speed of sound versus mole fraction of styrene + *n*-alkanols at 298.15 K. Symbols are the same as those in Figure 1.

styrene + methanol, + butan-1-ol, or + hexan-1-ol. These results show almost similar trends to those exhibited by the V^E results; that is, the values of Δk_S increase from methanol to hexan-1-ol, exhibiting slight positive values for hexan-1-ol-containing mixtures with a lower composition of styrene. The Benson and Kiyohara (1979) experimental plots of Δk_T versus Φ_1 for styrene + methanol, + butan-1-ol, or + pentan-1-ol mixtures are compared in Figure 7 with those calculated from the Flory theory (1965) at 298.15 K. The plots of Δu versus x_1 at 298.15 K, displayed in Figure 8, show a reverse trend to those of the V^E results.

Conclusions

An extensive experimental database on the binary mixtures of styrene + *n*-alkanols presented here can serve as a good experimental protocol to test the accuracy of the predictive equations. Experimental excess molar volume data agree better with the PFP theory than with the Flory theory. The Bloomfield and Dewan equation yields positive values of $\Delta \ln \eta$ for all the mixtures, whereas the experimentally calculated $\Delta \ln \eta$ values are negative in all cases except styrene + methanol. But the trends in their variations are identical. The Benson and Kiyohara (1979) values of Δk_S and the Flory (1965) Δk_T values show similar trends to the experimentally calculated values, but their magnitudes are different. The deviations in molar refraction and speed of sound show systematic effects with the size of *n*-alkanols.

Symbols

V^E = excess volume
$\Delta \ln \eta$ = deviations in logarithm of viscosity
Δk_S = deviations in isentropic compressibility
Δk_T = deviations in isothermal compressibility
u = speed of sound
P = pressure
T = temperature
V = volume
R = gas constant
x_i = mole fraction of the i-th component

Greek Letters

η = viscosity
ρ = density
σ = standard deviation
Φ_i = volume fraction of *i*-th component

Superscripts

E = excess value
0 = ideal state
* = characteristic state
~ = reduced state
m, mix = mixture properties
ideal = ideal properties

Subscripts

i = *i*-th component
1 = first component
2 = second component
exp = experimental
cal = calculated
obs = observed

Literature Cited

Abe, A.; Flory, P. J. The Thermodynamic Properties of Mixtures of Small, Nonpolar Molecules. *J. Am. Chem. Soc.* **1965**, *87*, 1838.

Aminabhavi, T. M.; Bindu, G. Density, Viscosity, Refractive Index and Speed of Sound of the Binary Mixtures of 2-Ethoxy ethanol with *n*-Alkanes (C_6-C_{12}), 2,2,4-Trimethylpentane and Cyclohexane in the Temperature Interval at 298.15−313.15 K. *J. Chem. Eng. Data* **1995**, *40*, 362−641.

Aminabhavi, T. M.; Patil, V. B. Density, Refractive Index, Viscosity, and Speed of Sound in Binary mixtures of Ethenylbenzene with Hexane, Heptane, Octane, Nonane, Decane, and Dodecane. *J. Chem. Eng. Data* **1997**, *42*, 641−646.

Aminabhavi, T. M.; Raikar, S. K.; Balundgi, R. H. Volumetric, Acoustic, Optical and Viscometric Properties of Binary Mixtures of 2-Methoxyethanol with Aliphatic Alcohols (C_1−C_8). *Ind. Eng. Chem. Res.* **1993**, *32*, 931−936.

Aminabhavi, T. M.; Bindu, G. Densities, Viscosities, Refractive Indices, and Speed of Sound of the Binary Mixtures of Bis(2-methoxy ethyl) ether with Nonane, Decane, Dodecane, Tetradecane, and Hexadecane at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1994**, *39*, 529−534.

Aralaguppi, M. I.; Aminabhavi, T. M.; Balundgi, R. H.; Joshi, S. S. Thermodynamic Interactions in Mixtures of Bromoform with Hydrocarbons. *J. Phys. Chem.* **1991**, *95*, 5299−5308.

Benson, G. C.; Kiyohara, O. Evaluation of Excess Isentropic Compressibilities and Isochoric Heat Capacities. *J. Chem. Thermodyn.* **1979**, *11*, 1061−1064.

Bloomfield, V. A.; Dewan, R. K. Viscosity of Liquid Mixtures. *J. Phys. Chem.* **1971**, *75*, 3113−3119.

Douheret, G.; Lajoie, P.; Davis, M. I.; Ratliff, J. L.; Ulloa, J.; Hoiland, H. Volumetric Properties of Binary Mixtures of Water with Methoxy-(ethoxy)$_n$ ethanols. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2291−2298.

Flory, P. J. Statistical Thermodynamics of Liquid Mixtures. *J. Am. Chem. Soc.* **1965,** *87*, 1833−1838.

Haijun. W.; Guokang, Z.; Mingzhi, C. Excess Volumes of (Acrylonitrile + an Aromatic Hydrocarbon at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994a**, *26*, 457−460.

Haijun, W.; Mingzhi, C.; Guokang, Z. Excess Volumes of an Aliphatic Dinitrile + an Aromatic Hydrocarbon at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1994b**, *26*, 913−918.

Haijun, W.; Mingzhi, C.; Guokang, Z. Excess Volumes of Benzonitrile + an Aromatic Hydrocarbon at the Temperature 298.15 K. *J. Chem. Thermodyn.* **1995a**, *27*, 57−61.

Haijun, W.; Chao, Z.; Mingzhi, C.; Hulin, L. Excess Volumes of a Polar Liquid + an Aromatic Hydrocarbon at the Temperature 298.15 K (*N*,*N*′- Dimethylformamide + an Aromatic Hydrocarbon). *J. Chem. Thermodyn.* **1995b**, *27*, 991−996.

Haijun, W.; Zhongxing, S.; Xiaoxin, Z. Excess Volumes of a Polar Liquid + an Aromatic Hydrocarbon at the Temperature 298.15 K (*N*,*N*′-Dimethylacetamide + an Aromatic Hydrocarbon). *J. Chem. Thermodyn.* **1995c**, *27*, 1349−1353.

Marquardt, D. W. An Algorithm for Least-squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431−441.

Miller, L, P.; Wachter, H. N.; Friend, V. Densities and Molar Volumes of Binary Solutions of Nitrobenzene in Electron Donating Solutions. *J. Chem. Eng. Data* **1975**, *20*, 417−419.

Ortega, J. Densities and Refractive Indices of Pure Alcohols at Several Temperatures. *J. Chem. Eng. Data* **1982**, *27*, 312−317.

Ortega, J.; Matos, J. S. Estimation of the Isobaric Expansivities from Several Equations of Molar Refraction for Some Pure Organic Compounds. *Mater. Chem. Phys.* **1986**, *15*, 415−425.

Patterson, D. Effect of Molecular Size and Shape in Solution Thermodynamics. *Pure Appl. Chem.* **1976**, *47*, 305−314.

Patterson, D.; Delmas, G. Molecular Weight Dependence of Lower and Upper Critical Solution Temperatures. *J. Polym. Sci., Part C* **1970**, *30*, 1−8.

Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

Reid, R. C.; Prausnitz, J. M.; Poling, B. E. The Properties of Gases and Liquids, 4th ed.; McGraw-Hill: New York, 1987; p 388.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Organic Solvents. Physical Properties and Methods of Purifications*; John Wiley & Sons: New York, 1986; Vol. II.

Vishwanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Hemisphere: New York, 1989.

Wilson, L.; Alencastro, R. B. D.; Sandorfy, C. Hydrogen Bonding of *n*-Alcohols of Different Chain Lengths. *Can. J. Chem.* **1985**, *63* (3), 40−45.

Won, Y. S.; Chang, D. K.; Mills, A. F. Density, Viscosity, Surface Tension, Carbon Dioxide Solubility, and Diffusivity of Methanol, Ethanol, Aqueous Propanol, and Aqueous Ethylene Glycol at 25 °C. *J. Chem. Eng. Data* **1981**, *26*, 140−141.

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