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Densities and Refractive Indices for 1-Hexene + *o*-Xylene, + *m*-Xylene, + *p*-Xylene, and + Ethylbenzene

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Densities and refractive indices were measured at 298.15 K for binary mixtures of 1-hexene + *o*-xylene, + *m*-xylene, + *p*-xylene, and + ethylbenzene over the entire composition range. The results were fitted to a polynomial relation to obtain the coefficients and standard errors. Excess volumes and molar refraction deviations were derived. Also, the refractive indices were compared with the predictions of the Lorentz−Lorenz, Gladstone−Dale, and Arago−Biot equations.

Introduction

Measurements of physical properties such as density and refractive index are helpful in understanding the thermodynamic properties of liquid mixtures. In this paper we present densities and refractive indices measured at 298.15 K for 1-hexene (1-HE) + *o*-xylene (OX), + *m*-xylene (MX), + *p*-xylene (PX), and + ethylbenzene (EB) as a function of the mole fraction at atmospheric pressure. These measurements have not been reported previously in the literature.

Experimental Section

Chemicals. The 1-hexene (>99.0 mol %) and *m*-xylene (>98.0 mol %) were supplied by Fluka, and *o*-xylene, *p*-xylene, and ethylbenzene were supplied by Merck with purities of 99.0 mol % or greater. All liquids were used without further purification. The purity of the liquids had been previously checked by gas chromatography.

Apparatus and Procedure. Mixtures of the required composition were prepared by mass using a Mettler AE 240 balance; the accuracy is within ±0.0001 g. The possible error in the mole fraction is estimated to be less than ±0.0002. The densities, ϱ, were measured using an Anton Paar DMA-46 vibrating-tube densimeter with a resolution of ±0.0001 $g\cdot cm^{-3}$. The refractive indices, n_D, have been measured with an automatic refractometer GPR 11-37-X Index with a resolution of ±0.000 01 unit. Calibration checks of the densimeter and refractometer were done routinely. A thermostatically controlled bath (Poly-Science Model 9610) was constant to ±0.02 K.

Results

Densities and refractive indices at 298.15 K are listed in Table 1. The densities and refractive indices of the mixtures were used to calculate the excess molar volumes, V_m^E

$$V_m^E = \sum_i x_i M_i (\varrho^{-1} - \varrho_i^{-1}) \qquad (1)$$

and the molar refraction deviations, δR_m where M_i represents the molar mass, x_i the mole fraction, ϱ_i the density, and n_{D_i} the refractive index of component i and ϱ the density and n_D represent the refractive index of the mixtures.

$$\delta R_m = \frac{\sum_i x_i M_i}{\varrho} \frac{n_D^2 - 1}{n_D^2 + 2} - \sum_i x_i \frac{M_i}{\varrho_i} \frac{n_{D_i}^2 - 1}{n_{D_i}^2 + 2} \qquad (2)$$

Table 1 shows the results obtained for excess molar volumes and excess molar refractions at 298.15 K for 1-hexene + *o*-xylene, + *m*-xylene, + *p*-xylene, and + ethylbenzene.

The excess properties, volume and molar refraction deviation, were fitted by the equation

$$Y^E/(\mathrm{cm^3 \cdot mol^{-1}}) = x_1(1 - x_1)\sum_{i=1}^{n} A_i (2x_1 - 1)^{i-1} \qquad (3)$$

where n is the polynomial degree. The parameters A_i and the standard deviations, σ, are given in Table 2. The polynomials of eq 3 were fitted to the results by the unweighted least-squares method. The degree of the equations was optimized by applyiny the F-test (*1*). The standard deviations were calculated by means of the equation

$$\sigma = [\sum_{i=1}^{N} (Y_{\mathrm{exptl}}^E - Y_{\mathrm{calcd}}^E)^2/(N - p)]^{1/2} \qquad (4)$$

where N is the number of experimental points and p is the number of estimated parameters.

Figures 1 and 2 show the excess molar volumes and the molar refraction deviation as a function of the mole fraction of 1-hexene.

For the prediction of refractive indices the following analytical expressions, based on the mixing rules compiled by Tasic et al. (*2*), have been used:

Lorentz−Lorenz equation

$$n_D = \left(\frac{2A + 1}{1 - A}\right)^{0.5} \qquad (5)$$

$$A = \left[\left(\frac{n_{D_1}^2 - 1}{n_{D_1}^2 + 2}\right)\frac{1}{\varrho_1} - \left(\frac{n_{D_1}^2 - 1}{n_{D_1}^2 + 2}\right)\frac{(1 - w_1)}{\varrho_1} + \left(\frac{n_{D_2}^2 - 1}{n_{D_2}^2 + 2}\right)\frac{(1 - w_1)}{\varrho_2}\right]\varrho \qquad (6)$$

where A is a parameter, w_1 is the mass fraction of the more volatile component, n_{D_1} and n_{D_2} are the refractive indices

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Table 1. Densities ϱ, Refractive Indices n_D, Excess Molar Volumes V_m^E, and Molar Refraction Deviations δR_m of Binary Systems at 298.15 K and Atmospheric Pressure

x	ϱ/($g\cdot cm^{-3}$)	n_D	V_m^E/($cm^3\cdot mol^{-1}$)	δR_m/($cm^3\cdot mol^{-1}$)	x	ϱ/($g\cdot cm^{-3}$)	n_D	V_m^E/($cm^3\cdot mol^{-1}$)	δR_m/($cm^3\cdot mol^{-1}$)
1-Hexene (1) + *o*-Xylene (2)									
0.0000	0.8741	1.501 77			0.5480	0.7633	1.439 20	−0.57	0.0716
0.1170	0.8512	1.488 85	−0.27	0.0241	0.6444	0.7432	1.427 87	−0.51	0.0731
0.1343	0.8477	1.486 91	−0.29	0.0300	0.6766	0.7364	1.424 06	−0.47	0.0745
0.1926	0.8361	1.480 31	−0.39	0.0368	0.7260	0.7261	1.418 20	−0.43	0.0689
0.2378	0.8270	1.475 16	−0.45	0.0432	0.7431	0.7225	1.416 15	−0.40	0.0667
0.2623	0.8220	1.472 37	−0.47	0.0491	0.7754	0.7157	1.412 36	−0.36	0.0676
0.3053	0.8133	1.467 43	−0.52	0.0529	0.8418	0.7018	1.404 45	−0.26	0.0563
0.3675	0.8006	1.460 24	−0.561	0.0587	0.8805	0.6937	1.399 80	−0.20	0.0459
0.4123	0.7914	1.455 05	−0.58	0.0631	0.9559	0.6780	1.390 70	−0.08	0.0169
0.4742	0.7786	1.447 97	−0.58	0.0770	0.9661	0.6758	1.389 47	−0.05	0.0162
0.5027	0.7727	1.444 51	−0.58	0.0703	1.0000	0.6688	1.385 39		
1-Hexene (1) + *m*-Xylene (2)									
0.0000	0.8596	1.494 43			0.5362	0.7589	1.434 48	−0.41	−0.1015
0.0482	0.8508	1.488 97	−0.08	−0.0176	0.5719	0.7521	1.430 58	−0.41	−0.1039
0.0718	0.8465	1.486 29	−0.12	−0.274	0.6357	0.7398	1.423 66	−0.39	−0.1003
0.1269	0.8363	1.480 06	−0.19	−0.0433	0.6799	0.7312	1.418 91	−0.36	−0.0927
0.2666	0.8102	1.464 34	−0.33	−0.0766	0.7342	0.7207	1.413 10	−0.33	−0.0857
0.2906	0.8057	1.461 65	−0.35	−0.0821	0.7922	0.7094	1.406 95	−0.27	−0.0724
0.3176	0.8006	1.458 63	−0.37	−0.0866	0.8426	0.6996	1.401 65	−0.22	−0.0600
0.3568	0.7932	1.454 27	−0.39	−0.0926	0.9095	0.6865	1.394 68	−0.13	−0.0369
0.4194	0.7813	1.447 32	−0.41	−0.0966	0.9389	0.6807	1.391 65	−0.08	−0.0232
0.4706	0.7715	1.441 67	−0.42	−0.1018	1.0000	0.6688	1.385 39		
0.5050	0.7649	1.437 89	−0.42	−0.1023					
1-Hexene (1) + *p*-Xylene (2)									
0.0000	0.8563	1.492 86			0.6523	0.7353	1.423 94	−0.33	0.0789
0.1305	0.8325	1.479 46	−0.15	0.0397	0.6730	0.7314	1.421 68	−0.33	0.0757
0.1479	0.8293	1.477 66	−0.16	0.0447	0.7296	0.7207	1.415 47	−0.30	0.0656
0.2244	0.8152	1.469 70	−0.22	0.0633	0.7619	0.7145	1.411 91	−0.27	0.0620
0.2796	0.8050	1.463 91	−0.26	0.0731	0.8453	0.6986	1.402 68	−0.21	0.0430
0.3053	0.8003	1.461 20	−0.29	0.0742	0.8981	0.6885	1.396 80	−0.16	0.0281
0.4130	0.7803	1.449 78	−0.34	0.0840	0.9219	0.6839	1.394 14	−0.12	0.0223
0.4765	0.7684	1.442 98	−0.35	0.0874	0.9458	0.6793	1.391 47	−0.09	0.0155
0.5227	0.7597	1.438 01	−0.35	0.0890	1.0000	0.6688	1.385 39		
0.5747	0.7500	1.432 39	−0.36	0.0837					
1-Hexene (1) + Ethylbenzene (2)									
0.0000	0.8624	1.492 98			0.5694	0.7531	1.432 54	−0.33	0.0725
0.0352	0.8558	1.489 31	−0.05	0.0065	0.6245	0.7423	1.426 57	−0.30	0.0730
0.0501	0.8530	1.487 76	−0.07	0.0096	0.6794	0.7316	1.420 61	−0.28	0.0687
0.0976	0.8440	1.482 79	−0.13	0.0199	0.7367	0.7204	1.414 36	−0.25	0.0621
0.1631	0.8315	1.475 91	−0.19	0.0345	0.7838	0.7112	1.409 21	−0.22	0.0544
0.2058	0.8234	1.471 41	−0.23	0.0400	0.8332	0.7015	1.403 79	−0.18	0.0461
0.2546	0.8140	1.466 25	−0.26	0.0501	0.8957	0.6892	1.396 91	−0.11	0.0335
0.2870	0.8078	1.462 81	−0.28	0.0536	0.9215	0.6842	1.394 07	−0.09	0.0243
0.3087	0.8036	1.460 50	−0.29	0.0573	0.9498	0.6786	1.390 94	−0.05	0.0180
0.4061	0.7848	1.450 11	−0.32	0.0675	1.0000	0.6688	1.385 39		
0.4530	0.7757	1.445 09	−0.33	0.0718					

of the pure components, and ϱ_1 and ϱ_2 the densities of the components.

Gladstone−Dale equation

$$n_D = \varrho\left[\frac{n_{D_1} - 1}{\varrho_1} - (n_{D_1} - 1)\frac{(1 - w_1)}{\varrho_1} + (n_{D_2} - 1)\frac{(1 - w_1)}{\varrho_2}\right] + 1 \qquad (7)$$

Arago−Biot equation

$$n_D = (n_{D_2} - n_{D_1})\frac{(1 - w_1)\varrho}{\varrho_2} + n_{D_1} \qquad (8)$$

The experimental refractive indices are compared in Table 3 to the predicted results for the Lorentz−Lorenz (L−L), Gladstone−Dale (G−D), and Arago−Biot (A−B) equations, and Figure 3 shows the deviations δ_{n_D} ($\delta_{n_D} = n_{D,exptl} - n_{D,calcd}$) plotted against the mole fraction of 1-hexene for all the mixtures, according to the mixing rules 6 and 7.

Conclusions

From Figure 1 it can be seen that the excess molar volumes are negative for all the mixtures; this may be attributed to interactions between the π electrons of the aromatic hydrocarbons and π' electrons of the olefin group. The excess molar volume increases when the size of substituents on the benzene ring increases. For various substituents of the same size, this property decreases with their relative proximity.

The δR_m are positive in the mixtures 1-hexene with *o*-xylene, *p*-xylene, or ethylbenzene and negative in the system 1-hexene + *m*-xylene (Figure 2). The predictions for refractive indices, according to the Arago−Biot mixing rule, are unsatisfactory for systems with a large change in volume on mixing, such as 1-hexene + *o*-xylene and

1-hexene + *m*-xylene. In this work, the Gladstone–Dale equation presents better results than the Lorentz–Lorenz equation, except for the system 1-hexene with *m*-xylene (Figure 3).

Registry Numbers Supplied by Author. 1-HE, 592-41-6; OX, 95-47-6; MX, 108-38-3; PX, 106-42-3; EB, 100-41-4.

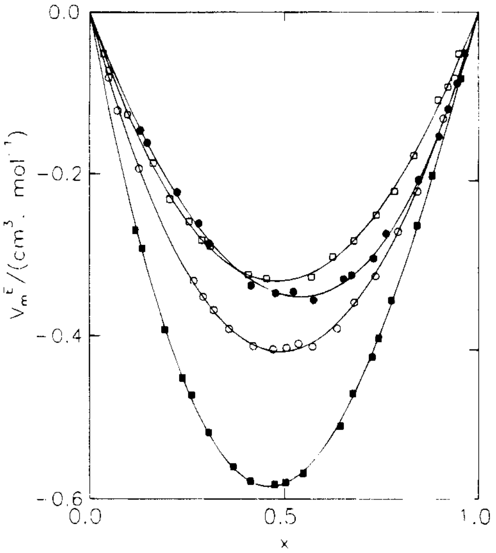

Figure 1. Excess molar volume at 298.15 K for 1-hexene with (■) *o*-xylene, (○) *m*-xylene, (●) *p*-xylene, and (□) ethylbenzene. *x* is the mole fraction of 1-hexene. The curves are calculated from the fitting of eq 3.

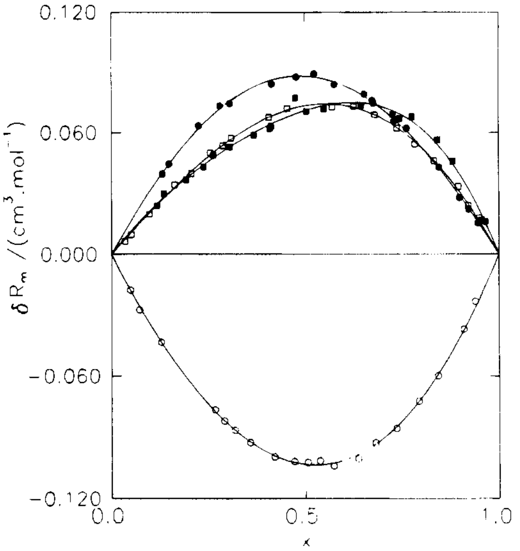

Figure 2. Molar refraction deviation at 298.15 K for 1-hexene with (■) *o*-xylene, (○) *m*-xylene, (●) *p*-xylene, and (□) ethylbenzene. *x* is the mole fraction of 1-hexene. The curves are calculated from the fitting of eq 3.

Table 2. Parameters and Standard Deviations, σ, of the Excess Molar Volumes and Molar Refraction Deviations for the Binary Mixtures from Eq 3

Y_m^E	A_1	A_2	A_3	σ
	1-Hexene (1) + *o*-Xylene (2)			
$V_m^E/(cm^3\cdot mol^{-1})$	−2.327	0.384	0.179	0.005
$\delta R_m/(cm^3\cdot mol^{-1})$	0.285	0.120	0.085	0.003
	1-Hexene (1) + *m*-Xylene (2)			
$V_m^E/(cm^3\cdot mol^{-1})$	−1.681	0.056	0.017	0.005
$\delta R_m/(cm^3\cdot mol^{-1})$	−0.413	−0.040	−0.012	0.001
	1-Hexene (1) + *p*-Xylene (2)			
$V_m^E/(cm^3\cdot mol^{-1})$	−1.403	−0.220	−0.054	0.005
$\delta R_m/(cm^3\cdot mol^{-1})$	0.351	−0.021	−0.023	0.001
	1-Hexene (1) + Ethylbenzene (2)			
$V_m^E/(cm^3\cdot mol^{-1})$	−1.325	0.104	−0.016	0.005
$\delta R_m/(cm^3\cdot mol^{-1})$	0.293	0.066	−0.008	0.001

Table 3. Standard Deviations, σ,[a] of Experimental Refraction Indices from Predicted Results for Various Equations

system	L–L[b]	G–D[c]	A–B[d]
1-hexene + *o*-xylene	0.000 84	0.000 21	0.003 17
1-hexene + *m*-xylene	0.001 17	0.001 79	0.004 25
1-hexene + *p*-xylene	0.000 95	0.000 34	0.001 68
1-hexene + ethylbenzene	0.000 74	0.000 18	0.001 59

[a] $\sigma = [\sum_{i=n}^{N}(n_{D,exptl} - n_{D,calcd})_i{}^2/N]^{1/2}$. [b] L–L = Lorentz–Lorenz equation. [c] G–D = Gladstone–Dale equation. [d] A–B = Arago–Biot equation.

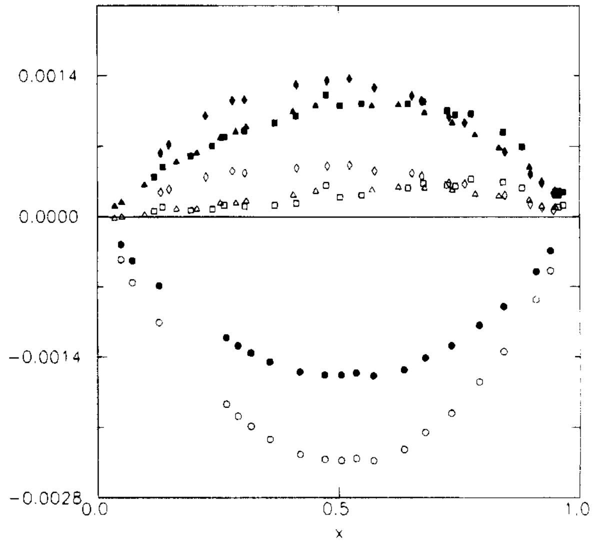

Figure 3. Variation of the refractive index (δn_D) with the mole fraction of 1-hexene at 298.15 K: 1-hexene + *o*-xylene (□, ■); 1-hexene + *m*-xylene (○, ●); 1-hexene + *p*-xylene (◇, ◆); 1-hexene + ethylbenzene (△, ▲). The open symbol corresponds to n_D calculated by the Gladstone–Dale equation; the closed symbol corresponds to n_D calculated by the Lorentz–Lorenz equation.

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