Density and Refractive Index of the Binary Mixtures of Cyclohexane with Dodecane, Tridecane, Tetradecane, and Pentadecane at (298.15, 303.15, and 308.15) K

T. M. Aminabhavi,* V. B. Patil, and M. I. Aralaguppi

Department of Chemistry, Karnatak University, Dharwad 580 003, India

J. D. Ortego and K. C. Hansen

Department of Chemistry, Lamar University, Beaumont, Texas 77710

Experimental values of density and refractive index are presented for the binary mixtures of cyclohexane with dodecane, tridecane, tetradecane, and pentadecane over the whole range of mixture compositions at (298.15, 303.15, and 308.15) K. These data are used to calculate the excess molar volume and deviations in molar refractivity. The excess quantities are fitted to the Redlich−Kister equation to estimate the values of the binary interaction parameters and values of the standard errors. The excess molar volume data at 298.15 K have been compared with the available literature findings for the mixtures of cyclohexane with dodecane and tetradecane.

Introduction

In our preceding paper (Aminabhavi et al., 1996), the experimental values of density, viscosity, and refractive index have been reported for the binary mixtures of cyclohexane with lower *n*-alkanes, viz., hexane to decane. In continuation of that study, we now present the experimental results of density, ρ, and refractive index, n_D, for the sodium D line for the binary mixtures of cyclohexane with higher *n*-alkanes, viz., dodecane (C_{12}), tridecane (C_{13}), tetradecane (C_{14}), and pentadecane (C_{15}), at (298.15, 303.15, and 308.15) K over the whole range of mixture compositions. From these data, the excess molar volume, V^E, and deviations in molar refractivity, ΔR, have been calculated. To calculate the molar refractivity, R_i of pure components and R_m of mixtures, we have employed the Lorentz−Lorenz and Eykman equations. The calculated quantities have been fitted to the Redlich−Kister equation (Redlich and Kister, 1948) using the multiparametric Marquardt algorithm (Marquardt, 1963) to estimate the required number of binary interaction parameters, A_i, and standard error values, σ. The equimolar V^E results of some of the systems studied in this paper are compared with the available literature data.

Experimental Section

Materials and Methods. Cyclohexane was purchased from BDH (London). The analytical grade dodecane, tridecane, tetradecane, and pentadecane were purchased from S. D. Fine Chemicals Ltd., Bombay. The solvents were used directly and their purity was ascertained by comparing their density and refractive index values with those in the literature (see Table 1). The GLC purity estimations of the liquids are also included in Table 1.

The preparations of the binary mixtures and mass, density, and refractive index measurements of the pure liquids and their binary mixtures are the same as described in the preceding paper (Aminabhavi et al., 1996).

* To whom all correspondences should be addressed. Fax: 91-836-347884.

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

	ρ/g·cm^{-3}		n_D		
liquid (mol % purity)	expt	lit.	expt	lit	ref
cyclohexane (>99.6)	0.7740	0.7739	1.4235	1.4235	Marsh, 1994
dodecane (>99.8)	0.7454	0.7452	1.4187	1.4195	Riddick et al., 1986
tridecane (>99.5)	0.7513	0.7527	1.4239	1.4235	Riddick et al., 1986
tetradecane (>99.4)	0.7596	0.7592	1.4263	1.4268	Marsh, 1994
pentadecane (>99.6)	0.7650	0.7649	1.4279	1.4297	Marsh, 1994

Results and Discussion

From the experimental values of ρ and n_D presented in Table 2, excess molar volume, V^E, and deviations in molar refractivity, ΔR, have been calculated as (Aminabhavi, 1994)

$$V^E/\text{cm}^3\cdot\text{mol}^{-1} = V_m - V_1x_1 - V_2x_2 \tag{1}$$

$$\Delta R/\text{cm}^3\cdot\text{mol}^{-1} = R_m - R_1\varphi_1 - R_2\varphi_2 \tag{2}$$

In the above equations, the terms V_i and V_m represent the molar volume of the ith component and of the mixture, respectively; x_i refers to mole fraction of the ith component of the mixture. Similarly, R_i and R_m are the molar refractivities of the individual components and of the mixture.

Following our earlier publications (Aminabhavi et al., 1994; Aminabhavi and Bindu, 1995), the volume fraction, φ_i, calculated using

$$\varphi_i = x_iV_i/\sum_{i=1}^{2}x_iV_i \tag{3}$$

was used to compute refractivities using the Lorentz−Lorenz and Eykman equations.

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Table 2. Experimental Densities (ρ) and Refractive Indices (n_D) of Binary Mixtures at Different Temperatures

	ρ/g·cm^{-3}			n_D		
x_1	298.15 K	303.15 K	308.15 K	298.15 K	303.15 K	308.15 K
Cyclohexane (1) + Dodecane (2)						
0.0000	0.7454	0.7417	0.7380	1.4207	1.4184	1.4163
0.1011	0.7463	0.7426	0.7389	1.4206	1.4181	1.4160
0.2067	0.7474	0.7436	0.7399	1.4205	1.4181	1.4157
0.3122	0.7489	0.7451	0.7413	1.4204	1.4180	1.4157
0.3979	0.7504	0.7465	0.7426	1.4202	1.4180	1.4156
0.4994	0.7522	0.7482	0.7443	1.4203	1.4181	1.4158
0.5973	0.7546	0.7505	0.7464	1.4203	1.4181	1.4160
0.6995	0.7575	0.7534	0.7495	1.4205	1.4182	1.4166
0.7985	0.7614	0.7570	0.7527	1.4208	1.4185	1.4168
0.8993	0.7666	0.7620	0.7575	1.4226	1.4199	1.4174
1.0000	0.7740	0.7692	0.7642	1.4235	1.4217	1.4175
Cyclohexane (1) + Tridecane (2)						
0.0000	0.7531	0.7494	0.7457	1.4239	1.4226	1.4200
0.1061	0.7536	0.7499	0.7462	1.4237	1.4219	1.4194
0.2108	0.7543	0.7506	0.7468	1.4234	1.4215	1.4189
0.3130	0.7551	0.7513	0.7476	1.4233	1.4208	1.4183
0.4183	0.7560	0.7521	0.7483	1.4230	1.4206	1.4179
0.5198	0.7573	0.7533	0.7491	1.4225	1.4204	1.4176
0.6181	0.7590	0.7549	0.7509	1.4224	1.4201	1.4172
0.7169	0.7610	0.7569	0.7528	1.4226	1.4201	1.4172
0.8048	0.7639	0.7596	0.7553	1.4227	1.4201	1.4173
0.9071	0.7677	0.7633	0.7587	1.4230	1.4203	1.4173
1.0000	0.7740	0.7692	0.7642	1.4235	1.4217	1.4175
Cyclohexane (1) + Tetradecane (2)						
0.0000	0.7596	0.7561	0.7525	1.4263	1.4248	1.4226
0.1058	0.7598	0.7561	0.7525	1.4261	1.4241	1.4222
0.2049	0.7600	0.7564	0.7526	1.4256	1.4236	1.4216
0.2965	0.7603	0.7568	0.7529	1.4251	1.4233	1.4206
0.3993	0.7607	0.7570	0.7532	1.4249	1.4231	1.4204
0.4614	0.7610	0.7572	0.7534	1.4243	1.4224	1.4198
0.6067	0.7622	0.7584	0.7545	1.4237	1.4219	1.4192
0.7015	0.7637	0.7596	0.7555	1.4233	1.4207	1.4179
0.7992	0.7655	0.7614	0.7571	1.4231	1.4205	1.4177
0.9109	0.7691	0.7647	0.7602	1.4224	1.4197	1.4173
1.0000	0.7740	0.7692	0.7642	1.4235	1.4217	1.4175
Cyclohexane (1) + Pentadecane (2)						
0.0000	0.7650	0.7614	0.7579	1.4279	1.4256	1.4238
0.0970	0.7648	0.7612	0.7577	1.4279	1.4254	1.4236
0.2040	0.7647	0.7611	0.7574	1.4272	1.4249	1.4226
0.3045	0.7647	0.7611	0.7573	1.4257	1.4238	1.4218
0.3943	0.7648	0.7612	0.7574	1.4252	1.4234	1.4208
0.4690	0.7648	0.7610	0.7573	1.4246	1.4228	1.4200
0.6004	0.7654	0.7616	0.7576	1.4238	1.4213	1.4198
0.6965	0.7661	0.7622	0.7582	1.4233	1.4204	1.4183
0.7988	0.7674	0.7633	0.7590	1.4226	1.4202	1.4176
0.9004	0.7697	0.7652	0.7608	1.4213	1.4188	1.4166
1.0000	0.7740	0.7692	0.7642	1.4235	1.4217	1.4175

The results of V^E and ΔR have been fitted to the Redlich–Kister equation (Redlich and Kister, 1948) to estimate the coefficients, A_i, and standard errors, σ (Aminabhavi and Bindu, 1995). These results are presented in Table 3.

The results of V^E versus x_1 at 298.15 K given in Figure 1 are positive over the entire range of compositions. These positive V^E values show a systematic increase from dodecane to pentadecane, thus exhibiting the chain length effect of alkanes on V^E results. Upon comparison of equimolar V^E results at 298.15 K with those of the published results of Awwad and Salman (1986) for mixtures of cyclohexane with dodecane and tetradecane, we find that our $V^E = 0.530$ cm^3·mol^{-1} for the cyclohexane + dodecane mixture is 6.7% lower than the literature V^E value of 0.568 cm^3·mol^{-1}. For the cyclohexane + tetradecane mixture, our $V^E = 0.630$ cm^3·mol^{-1} is about 2.8% higher than the published value of 0.613 cm^3·mol^{-1}. The effect of temperature on V^E shows a systematic decrease with increasing temperature. However, this dependence is not displayed graphically to avoid overcrowding of graphs.

Table 3. Estimated Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ
Cyclohexane (1) + Dodecane (2)					
$V^E/10^6$(m^3·mol^{-1})	298.15	2.082	−0.927	0.873	0.012
	303.15	2.023	−0.959	0.775	0.016
	308.15	1.923	−0.788	0.727	0.021
$\Delta R_{LL}/10^6$(m^3·mol^{-1})	298.15	−21.38	8.034	−2.610	0.027
	303.15	−21.37	7.815	−3.063	0.026
	308.15	−21.04	8.243	−3.195	0.019
$\Delta R_{EYK}/10^6$(m^3·mol^{-1})	298.15	−47.25	17.76	−5.695	0.061
	303.15	−47.21	17.24	−6.768	0.058
	308.15	−46.42	18.26	−7.088	0.043
Cyclohexane (1) + Tridecane (2)					
$V^E/10^6$(m^3·mol^{-1})	298.15	2.292	−1.199	0.768	0.030
	303.15	2.252	−1.251	0.396	0.028
	308.15	2.155	−1.158	0.260	0.043
$\Delta R_{LL}/10^6$(m^3·mol^{-1})	298.15	−26.44	10.87	−4.261	0.028
	303.15	−26.72	11.01	−5.242	0.039
	308.15	−26.53	11.11	−4.568	0.035
$\Delta R_{EYK}/10^6$(m^3·mol^{-1})	298.15	−58.46	24.05	−9.369	0.061
	303.15	−59.12	24.36	−11.69	0.088
	308.15	−58.64	24.62	−10.09	0.076
Cyclohexane (1) + Tetradecane (2)					
$V^E/10^6$(m^3·mol^{-1})	298.15	2.448	−1.204	0.682	0.013
	303.15	2.352	−1.202	0.658	0.027
	308.15	2.234	−1.020	0.729	0.013
$\Delta R_{LL}/10^6$(m^3·mol^{-1})	298.15	−32.13	13.90	−6.632	0.034
	303.15	−32.32	13.71	−7.144	0.058
	308.15	−32.27	14.05	−6.504	0.049
$\Delta R_{EYK}/10^6$(m^3·mol^{-1})	298.15	−71.10	30.72	−14.69	0.075
	303.15	−71.54	30.27	−15.90	0.132
	308.15	−71.39	31.07	−14.38	0.111
Cyclohexane (1) + Pentadecane (2)					
$V^E/10^6$(m^3·mol^{-1})	298.15	2.526	−1.182	0.834	0.014
	303.15	2.421	−1.043	0.977	0.025
	308.15	2.348	−0.956	0.767	0.022
$\Delta R_{LL}/10^6$(m^3·mol^{-1})	298.15	−38.31	17.46	−9.522	0.036
	303.15	−38.42	17.11	−8.978	0.043
	308.15	−38.21	17.49	−9.211	0.050
$\Delta R_{EYK}/10^6$(m^3·mol^{-1})	298.15	−84.84	38.61	−21.14	0.080
	303.15	−85.08	37.76	−19.86	0.095
	308.15	−84.56	38.66	−20.41	0.112

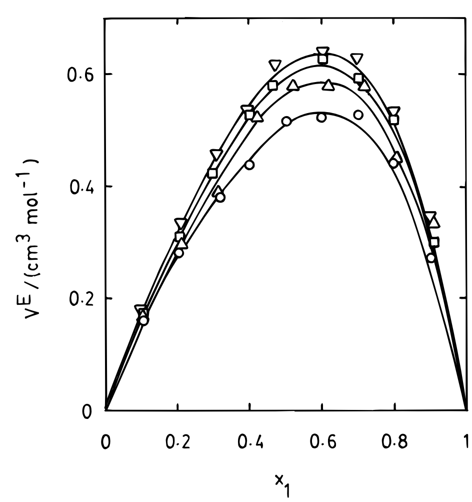

Figure 1. Excess molar volume vs mole fraction at 298.15 K for mixtures of cyclohexane with (○) dodecane, (△) tridecane, (□) tetradecane, and (▽) pentadecane.

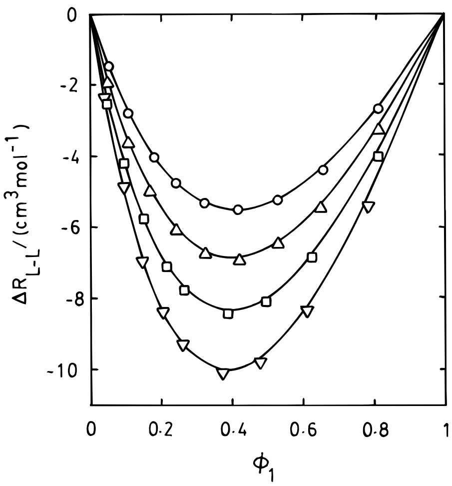

Figure 2. Deviations in molar refractivity (Lorentz−Lorenz) vs volume fraction at 298.15 K for the binary mixtures given in Figure 1.

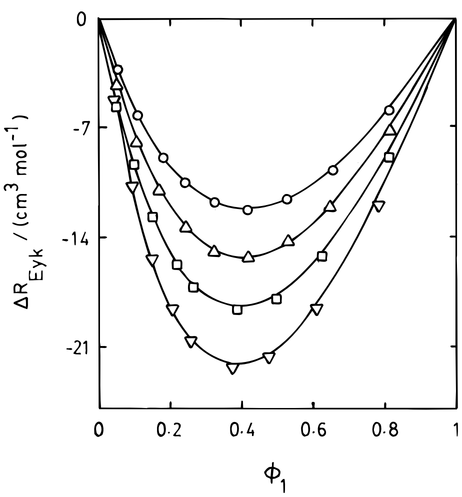

Figure 3. Deviations in molar refractivity (Eykman) vs volume fraction at 298.15 K for the binary mixtures given in Figure 1.

The changes in molar refractivity at 298.15 K computed from Lorentz−Lorenz and Eykman equations are presented in Figures 2 and 3, respectively. These results are negative and decrease systematically with an increase in chain length of *n*-alkanes from dodecane to pentadecane. On the other hand, the results of ΔR do not exhibit any systematic effect on temperature. However, the experimental data of density and refractive index for the present mixtures at higher temperatures are not available in the literature with which we can compare our results.

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