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Thermodynamic and Transport Properties of Binary Mixtures Containing 1,3-Dioxolane

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This paper reports density and viscosity measurements for the binary mixtures of cyclopentane or cyclohexane or benzene with 1,3-dioxolane at 283.15, 298.15, and 313.15 K. From the experimental data, excess volumes and excess viscosities were calculated and the results were fitted to a Redlich–Kister-type equation. The results are discussed in terms of molecular interactions. The Prigogine–Flory–Patterson and Blomfield–Dewan theories were used to analyze the results at 298.15 K.

KEY WORDS: benzene; cyclohexane; cyclopentane; density; 1,3-dioxolane; viscosity.

1. INTRODUCTION

The comparative study of mixing properties of the systems cycloalkane–heterocycle and benzene–heterocycle can give information not only on the existence of specific interactions between the components of the mixture but also on the nature of the interactions in the pure heterocycle. With this aim we have previously investigated several systems containing cyclohexane or benzene and a heterocycle [1–5], and this paper is a continuation of these studies.

We present here density and viscosity measurements for the mixtures cyclopentane or cyclohexane or benzene with 1,3-dioxolane at 283.15, 298.15, and 313.15 K along with their calculated excess volumes and excess viscosities. To our knowledge there are neither density nor viscosity measurements in the literature for these mixtures.

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From a quantitative point of view we have applied the Prigogine–Flory–Patterson and Bloomfield–Dewan theories to the experimental data at 298.15 K.

2. EXPERIMENTAL

Cyclopentane (purity better than 99 mol%) was obtained from Merck; cyclohexane and benzene (purities better than 99.9 mol%) and 1,3-dioxolane (purity better than 99.5 mol%) were provided by Aldrich. The purities of these compounds were checked by a chromatographic method, confirming the absence of other significant organic components. All liquids were used without further purification.

Densities were measured with an Anton–Paar DMA-58 vibrating tube densimeter, and kinematic viscosities were determined using an Ubbelohde viscometer with a Schott–Geräte automatic measuring unit, Model AVS-440. Details of the calibration and experimental procedures and of the accuracy of the measurements have been reported previously [6].

The mixtures were prepared using a Mettler H20T balance. The possible error in the mole fractions is estimated to be less than ±0.0001.

Table I shows the experimental values of density and viscosity for the pure compounds at 298.15 K compared with the published values [7–10]. These results agree reasonably well with the values given in the literature.

3. RESULTS AND DISCUSSION

From the measured density, ρ, and kinematic viscosity, ν, the absolute viscosity, η, can be obtained ($\eta = \rho\nu$). The experimental values of density and viscosity for the binary mixtures are given in Tables II and III, respectively.

Table I. Densities, ρ, and Viscosities, η, of Pure Compounds at 298.15 Compared with Literature Data

	ρ (g · cm^{-3})		η (mPa · s)	
Compound	Expt.	Lit.	Expt.	Lit.
Cyclopentane	0.73969	0.7403 [7]	0.4169	0.416 [9]
Cyclohexane	0.77387	0.77381 [8]	0.8951	0.8950 [8]
Benzene	0.87355	0.87360 [9]	0.6090	0.6028 [9]
1,3-Dioxolane	1.05880	1.05877 [10]	0.5919	

Table II. Densities, ρ, and Excess Volumes, V^{E}, of the Binary Mixtures Studied at Between 283.15 and 313.15 K

x_1	ρ (g·cm^{-3})	V^{E} (cm^3·mol^{-1})	x_1	ρ (g·cm^{-3})	V^{E} (cm^3·mol^{-1})
Cyclopentane(1) + 1,3-dioxolane(2) at 283.15 K					
0.0000	1.07714	0.0000	0.5966	0.85733	0.4924
0.0991	1.03352	0.1332	0.6995	0.82826	0.4557
0.2018	0.99155	0.2644	0.8007	0.80190	0.3466
0.3021	0.95379	0.3554	0.8969	0.77844	0.2032
0.3996	0.91962	0.4241	1.0000	0.75492	0.0000
0.4984	0.88720	0.4818			
Cyclopentane(1) + 1,3-dioxolane(2) at 298.15 K					
0.0000	1.05880	0.0000	0.5924	0.84075	0.6445
0.0985	1.01554	0.1500	0.6997	0.81087	0.6005
0.2011	0.97376	0.2980	0.7953	0.78646	0.4751
0.3008	0.93612	0.4264	0.9020	0.76119	0.2652
0.3990	0.90181	0.5190	1.0000	0.73969	0.0000
0.4978	0.86950	0.6031			
Cyclopentane(1) + 1,3-dioxolane(2) at 313.15 K					
0.0000	1.04019	0.0000	0.5928	0.82354	0.7317
0.0996	0.99679	0.1588	0.6980	0.79469	0.6809
0.2014	0.95523	0.3506	0.7955	0.77004	0.5605
0.3001	0.91826	0.4906	0.8998	0.74576	0.3402
0.3997	0.88348	0.6233	1.0000	0.72455	0.0000
0.5137	0.84704	0.7067			
Cyclohexane(1) + 1,3-dioxolane(2) at 283.15 K					
0.0000	1.07714	0.0000	0.5956	0.86755	0.8668
0.0995	1.03093	0.2686	0.7036	0.84252	0.7909
0.2015	0.98909	0.5068	0.8011	0.82209	0.6699
0.3011	0.95325	0.6623	0.9002	0.80386	0.4072
0.3991	0.92177	0.7669	1.0000	0.78776	0.0000
0.5025	0.89179	0.8487			
Cyclohexane(1) + 1,3-dioxolane(2) at 298.15 K					
0.0000	1.05880	0.0000	0.5963	0.85172	0.9398
0.1000	1.01288	0.2885	0.6985	0.82824	0.8855
0.2006	0.97191	0.5549	0.8008	0.80738	0.7254
0.2985	0.93700	0.7282	0.8951	0.79037	0.4604
0.3984	0.90534	0.8428	1.0000	0.77387	0.0000
0.5004	0.87625	0.9237			

Table II. *(Continued)*

x_1	ρ $(\mathrm{g \cdot cm^{-3}})$	V^E $(\mathrm{cm^3 \cdot mol^{-1}})$	x_1	ρ $(\mathrm{g \cdot cm^{-3}})$	V^E $(\mathrm{cm^3 \cdot mol^{-1}})$
Cyclohexane(1) + 1,3-dioxolane(2) at 313.15 K					
0.0000	1.04019	0.0000	0.5959	0.83553	1.0466
0.1008	0.99433	0.3166	0.6990	0.81252	0.9593
0.1998	0.95450	0.5950	0.8009	0.79227	0.7744
0.3008	0.91838	0.8412	0.9012	0.77476	0.4528
0.3970	0.88811	0.9871	1.0000	0.75957	0.0000
0.4985	0.85961	1.0747			
Benzene(1) + 1,3-dioxolane(2) at 283.15 K					
0.0000	1.07714	0.0000	0.6135	0.95259	−0.0927
0.0984	1.05456	−0.0248	0.7116	0.93569	−0.0864
0.2013	1.03215	−0.0488	0.7941	0.92200	−0.0754
0.2909	1.01351	−0.0640	0.9002	0.90499	−0.0475
0.3915	0.99355	−0.0796	1.0000	0.88950	0.0000
0.5067	0.97180	−0.0909			
Benzene(1) + 1,3-dioxolane(2) at 298.15 K					
0.0000	1.05880	0.0000	0.6097	0.93655	−0.1029
0.0999	1.03615	−0.0252	0.7107	0.91939	−0.0994
0.2036	1.01386	−0.0498	0.8016	0.90448	−0.0828
0.3043	0.99329	−0.0700	0.9008	0.88875	−0.0496
0.3902	0.97654	−0.0859	1.0000	0.87355	0.0000
0.4924	0.95744	−0.0982			
Benzene(1) + 1,3-dioxolane(2) at 313.15 K					
0.0000	1.04019	0.0000	0.6178	0.91820	−0.1120
0.1043	1.01684	−0.0254	0.7082	0.90303	−0.1053
0.2013	0.99628	−0.0499	0.8001	0.88811	−0.0844
0.2996	0.97643	−0.0708	0.9003	0.87243	−0.0496
0.3962	0.95788	−0.0922	1.0000	0.85738	0.0000
0.4989	0.93902	−0.1069			

Excess volumes and excess viscosities were calculated from density and viscosity data according to the following equations:

$$V^E = x_1 M_1[(1/\rho)-(1/\rho_1)] + x_2 M_2[(1/\rho)-(1/\rho_2)] \qquad (1)$$

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2) \qquad (2)$$

where M_i, ρ_i, η_i, and x_i designate the molar mass $(\mathrm{g \cdot mol^{-1}})$, density $(\mathrm{g \cdot cm^{-3}})$, viscosity $(\mathrm{mPa \cdot s})$, and molar fraction of component i in the

Table III. Viscosities, η, and Excess Viscosities, η^E, of the Binary Mixtures Studied at Between 283.15 and 313.15 K

x_1	η (mPa·s)	η^E (mPa·s)	x_1	η (mPa·s)	η^E (mPa·s)
Cyclopentane(1) + 1,3-dioxolane(2) at 283.15 K					
0.0000	0.7077	0.0000	0.5979	0.5177	−0.0623
0.0988	0.6582	−0.0284	0.7027	0.5015	−0.0561
0.1997	0.6186	−0.0465	0.7987	0.4924	−0.0447
0.3005	0.5864	−0.0571	0.8995	0.4879	−0.0276
0.3997	0.5601	−0.0622	1.0000	0.4941	0.0000
0.4992	0.5370	−0.0641			
Cyclopentane(1) + 1,3-dioxolane(2) at 298.15 K					
0.0000	0.5919	0.0000	0.5979	0.4340	−0.0532
0.0988	0.5513	−0.0233	0.7027	0.4216	−0.0473
0.1997	0.5176	−0.0394	0.7987	0.4149	−0.0372
0.3005	0.4908	−0.0485	0.8995	0.4124	−0.0221
0.3997	0.4685	−0.0535	1.0000	0.4169	0.0000
0.4992	0.4495	−0.0551			
Cyclopentane(1) + 1,3-dioxolane(2) at 313.15 K					
0.0000	0.5000	0.0000	0.5979	0.3679	−0.0451
0.0988	0.4666	−0.0190	0.7027	0.3581	−0.0397
0.1997	0.4380	−0.0329	0.7987	0.3520	−0.0318
0.3005	0.4150	−0.0413	0.8995	0.3510	−0.0182
0.3997	0.3968	−0.0451	1.0000	0.3545	0.0000
0.4992	0.3804	−0.0470			
Cyclohexane(1) + 1,3-dioxolane(2) at 283.15 K					
0.0000	0.7077	0.0000	0.5974	0.8307	−0.1563
0.0994	0.7079	−0.0463	0.6998	0.8766	−0.1583
0.1978	0.7179	−0.0823	0.8012	0.9441	−0.1382
0.3014	0.7387	−0.1099	0.8994	1.0325	−0.0957
0.3991	0.7630	−0.1313	1.0000	1.1753	0.0000
0.4961	0.7939	−0.1457			
Cyclohexane(1) + 1,3-dioxolane(2) at 298.15 K					
0.0000	0.5919	0.0000	0.5974	0.6642	−0.1088
0.0994	0.5886	−0.0334	0.6998	0.6971	−0.1070
0.1978	0.5930	−0.0589	0.8012	0.7404	−0.0944
0.3014	0.6047	−0.0786	0.8994	0.8026	−0.0620
0.3991	0.6199	−0.0930	1.0000	0.8951	0.0000
0.4961	0.6405	−0.1018			

Table III. *(Continued)*

x_1	η (mPa · s)	η^E (mPa · s)	x_1	η (mPa · s)	η^E (mPa · s)
Cyclohexane(1) + 1,3-dioxolane(2) at 313.15 K					
0.0000	0.5000	0.0000	0.5974	0.5441	−0.0756
0.0994	0.4948	−0.0251	0.6998	0.5653	−0.0749
0.1978	0.4959	−0.0437	0.8012	0.5967	−0.0638
0.3014	0.5024	−0.0581	0.8994	0.6392	−0.0410
0.3991	0.5119	−0.0681	1.0000	0.7003	0.0000
0.4961	0.5256	−0.0738			
Benzene(1) + 1,3-dioxolane(2) at 283.15 K					
0.0000	0.7077	0.0000	0.5985	0.7452	0.0044
0.1006	0.7141	0.0008	0.6993	0.7505	0.0041
0.1994	0.7204	0.0017	0.7998	0.7552	0.0033
0.2990	0.7268	0.0026	0.8987	0.7596	0.0022
0.3987	0.7331	0.0034	1.0000	0.7630	0.0000
0.5003	0.7396	0.0042			
Benzene(1) + 1,3-dioxolane(2) at 298.15 K					
0.0000	0.5919	0.0000	0.6016	0.6064	0.0042
0.0968	0.5944	0.0008	0.7040	0.6079	0.0040
0.1990	0.5970	0.0017	0.7993	0.6089	0.0033
0.3032	0.5997	0.0026	0.8946	0.6094	0.0022
0.4021	0.6022	0.0034	1.0000	0.6090	0.0000
0.5050	0.6045	0.0040			
Benzene(1) + 1,3-dioxolane(2) at 313.15 K					
0.0000	0.5000	0.0000	0.5985	0.4998	0.0040
0.1006	0.5001	0.0008	0.6993	0.4988	0.0037
0.1994	0.5003	0.0017	0.7998	0.4976	0.0032
0.2990	0.5005	0.0026	0.8987	0.4959	0.0022
0.3987	0.5005	0.0033	1.0000	0.4930	0.0000
0.5003	0.5004	0.0039			

mixture, respectively. Quantities without subscripts refer to the mixture. These functions, i.e., excess volumes and excess viscosities, are presented in Tables II and III and plotted in Figs. 1 to 3.

The values of V^E and η^E were fitted by the Redlich–Kister equation:

$$Y^E = x_1(1-x_1) \sum_{i=0}^{i=n} A_i(2x_1-1)^i \qquad (3)$$

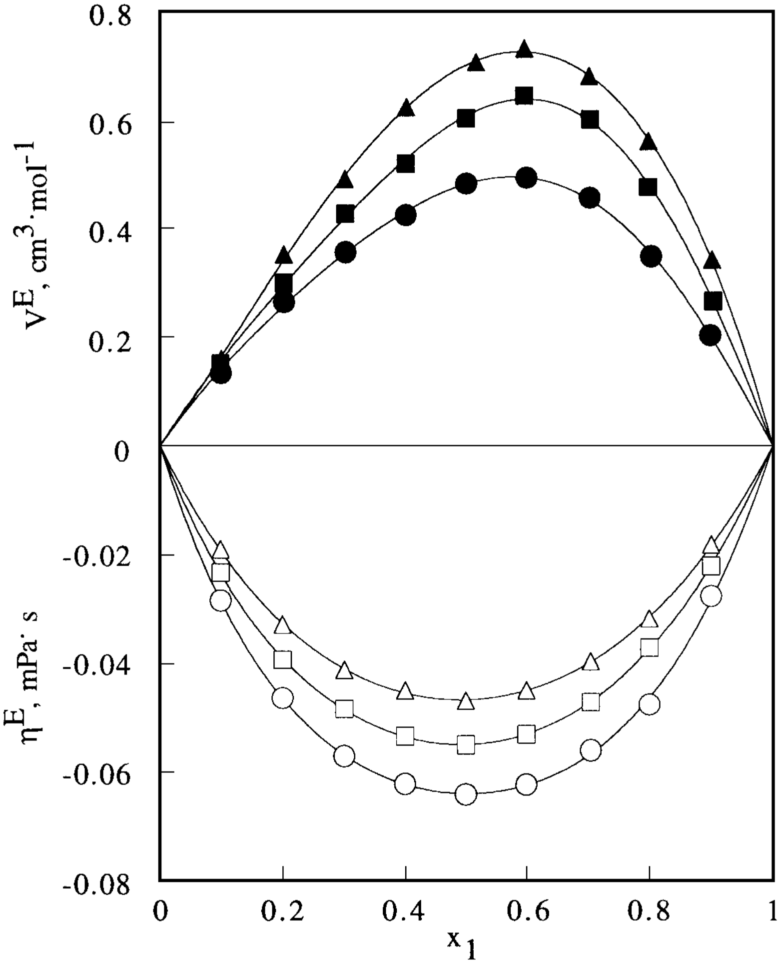

Fig. 1. Excess properties of cyclopentane(1) + 1,3-dioxolane(2) as a function of mole fraction x_1 at several temperatures: $T = 283.15$ K (○); $T =$ 298.15 K (□); $T = 313.15$ K (△). Filled symbols, V^E; open symbols, η^E. (——) Redlich–Kister equations.

where A_i's are adjustable parameters and x_1 is the mole fraction of the hydrocarbon. The values of these parameters are given in Table IV, together with the corresponding standard deviations.

The excess volumes for mixtures containing cyclopentane and cyclohexane attain very large positive values and these values increase with increasing temperature, with cyclopentane having the larger temperature

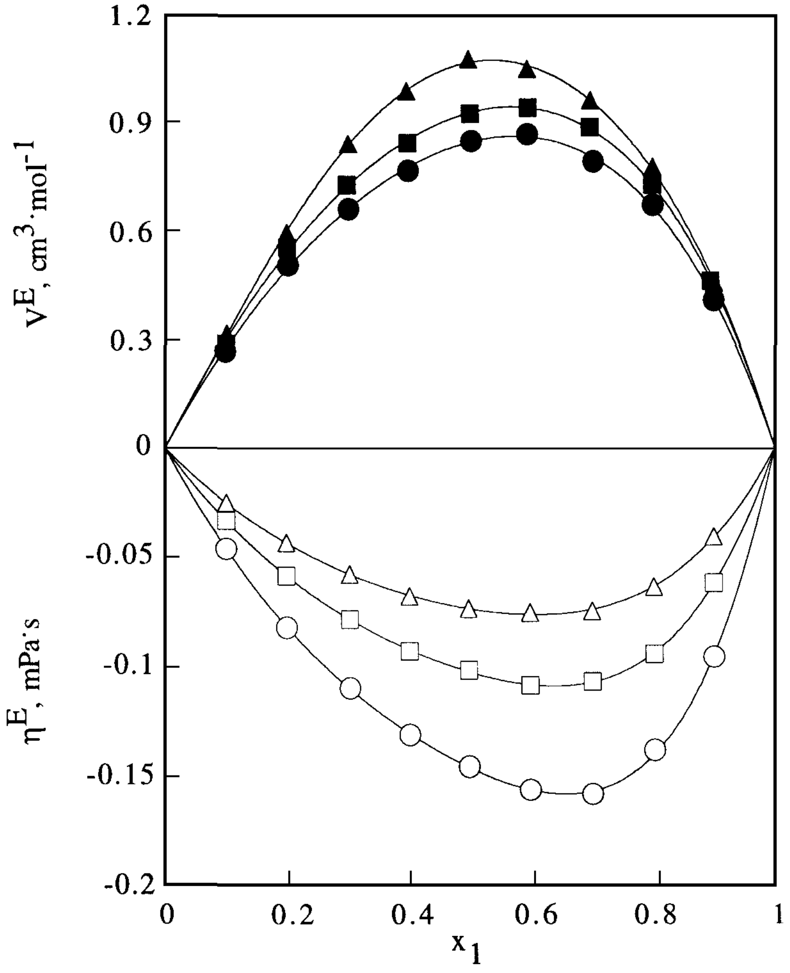

Fig. 2. Excess properties of cyclohexane(1) + 1,3-dioxolane(2) as a function of mole fraction x_1 at several temperatures: $T = 283.15$ K (○); $T = 298.15$ K (□); $T = 313.15$ K (△). Filled symbols, V^E; open symbols, η^E. (——) Redlich–Kister equations.

coefficient. The influence of the ring size of the cycloalkane can also be noted, as the V^E values for cyclopentane are smaller than those for cyclohexane. On the other hand, V^E values for mixtures containing benzene are negative and increase in absolute value with increasing temperature. Positive V^E values for the mixtures containing cyclopentane and cyclohexane can be largely explained by the weakening of the dipole–dipole interactions in the pure 1,3-dioxolane in the mixing process. The subsequent

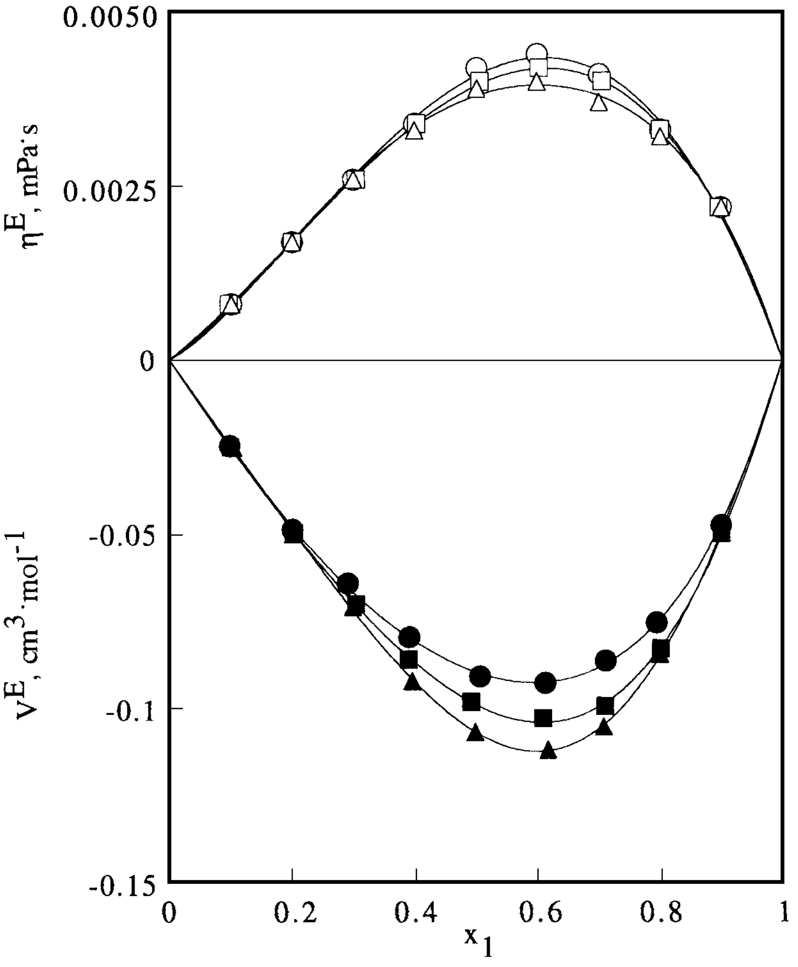

Fig. 3. Excess properties of benzene(1) + 1,3-dioxolane(2) as a function of mole fraction x_1 at several temperatures: $T = 283.15$ K (○); $T = 298.15$ K (□); $T =$ 313.15 K (△). Filled symbols, V^E; open symbol, η^E. (——) Redlich–Kister equations.

breaking of the molecular order increases the volume of the mixture. Negative V^E values for the benzene + 1,3-dioxolane mixture can be explained in terms of specific n–π interactions between the oxygen atom of 1,3-dioxolane and the aromatic ring of benzene [11]. The presence of these interactions offsets the positive contributions to V^E and leads to negative excess volumes.

The excess viscosities show also different behavior for mixtures containing either a cycloalkane or benzene. For cycloalkanes, η^E values are

Table IV. Coefficients, A_i, and Standard Deviations, σ, in Eq. (3)

Function	T (K)	A_0	A_1	A_2	A_3	σ
		Cyclopentane + 1,3-dioxolane				
V^E (cm$^3 \cdot$ mol^{-1})	283.15	1.9252	0.6531	−0.0797	−0.4150	0.0060
	298.15	2.4346	1.1638	−0.1103	−0.6220	0.0075
	313.15	2.8104	1.0556	−0.0372	0.2200	0.0068
η^E (mPa $\cdot$ s)	283.15	−0.2560	0.0072	−0.0839		0.0004
	298.15	−0.2202	0.0092	−0.0517		0.0003
	313.15	−0.1873	0.0067	−0.0358		0.0003
		Cyclohexane + 1,3-dioxolane				
V^E (cm$^3 \cdot$ mol^{-1})	283.15	3.3792	0.8837	0.6844		0.0091
	298.15	3.7046	0.9517	0.7154		0.0096
	313.15	4.2664	0.6178	0.0486	0.6919	0.0086
η^E (mPa $\cdot$ s)	283.15	−0.5867	−0.2620	−0.3063	−0.1073	0.0012
	298.15	−0.4115	−0.1629	−0.1892	−0.0530	0.0005
	313.15	−0.2960	−0.0911	−0.1147	−0.0312	0.0006
		Benzene + 1,3-dioxolane				
V^E (cm$^3 \cdot$ mol^{-1})	283.15	−0.3584	−0.1215	−0.0657	−0.0471	0.0009
	298.15	−0.3958	−0.1777	−0.0419		0.0008
	313.15	−0.4278	−0.2122	0.0263	0.0636	0.0008
η^E (mPa $\cdot$ s)	283.15	0.0164	0.0089	−0.0011	0.0001	0.0001
	298.15	0.0158	0.0084	0.0001	0.0005	0.0000
	313.15	0.0152	0.0060	0.0009	0.0054	0.0001

negative and decrease in absolute value as the temperature is increased, with these values more negative for cyclohexane. With respect to mixtures containing benzene, η^E values are slightly positive and the temperature coefficient is negative and very small. For mixtures containing cycloalkanes, specific interactions with 1,3-dioxolane are not important and the predominant effect is the weakening of the dipole–dipole interactions in 1,3-dioxolane. Thus, for this kind of mixtures η^E values are found to be negative, whereas the existence of charge–transfer interactions leading to the formation of complex species between the two components is indicated by positive η^E values as for the benzene + 1,3-dioxolane mixture.

4. THEORETICAL ANALYSIS

4.1. Prigogine–Flory–Patterson Theory

According to the Prigogine–Flory–Patterson model of solutions [12, 13], V^E can be calculated from the equation

$$\frac{V^{\mathrm{E}}}{x_1 V_1^* + x_2 V_2^*} = \frac{(\tilde{V}^{1/3}-1)\,\tilde{V}^{2/3}}{(4/3)\,\tilde{V}^{-1/3}-1}\,\Psi_1 \theta_2 \frac{X_{12}}{P_1^*} - \frac{(\tilde{V}_1-\tilde{V}_2)^2\,[(14/9)\,\tilde{V}^{-1/3}-1]}{[(4/3)\,\tilde{V}^{-1/3}-1]\,\tilde{V}}\,\Psi_1 \Psi_2 + \frac{(\tilde{V}_1-\tilde{V}_2)}{P_1^* \Psi_2 + P_2^* \Psi_1}\,(P_1^* - P_2^*)\,\Psi_1 \Psi_2 \qquad (4)$$

where the contact energy fraction Ψ_1 is given by

$$\Psi_1 = 1 - \Psi_2 = \frac{\phi_1 P_1^*}{\phi_1 P_1^* + \phi_2 P_2^*} \qquad (5)$$

and all other parameters pertain to the Flory theory [14, 15]. The first term in Eq. (4) is the interaction contribution, ΔV_{int}, the second term is the free volume contribution, ΔV_{fv}, and the third term is the internal pressure contribution, ΔV_{P}^*.

Flory parameters of the pure compounds along with their physical properties are listed in Table V. Thermal expansion coefficients, α, were derived from the measured densities in this laboratory. Isothermal compressibilities, κ_{T}, were calculated from α, the experimental isentropic compressibilities, κ_{S}, and the molar heat capacities, C_{p} [16].

To solve Eq. (4), it is necessary to obtain values for the interaction parameter X_{12}, values that were derived by fitting the theory to experimental equimolecular H^{E} values for each of the three systems [19–21]. Table VI gives the obtained interaction parameters, the calculated values of the three contributions to the equimolecular excess volume according to Eq. (4), and the experimental and theoretical V^{E} values.

For the mixtures involving a cycloalkane, the interaction contribution is large and positive and is the dominant term. The free volume and internal

Table V. Physical Properties and Flory Parameters of the Pure Compounds at 298.15 K

Compound	V ($\mathrm{cm^3 \cdot mol^{-1}}$)	$\alpha \times 10^3$ ($\mathrm{K^{-1}}$)	κ_{T} ($\mathrm{TPa^{-1}}$)	$\tilde{V}$	P^* ($\mathrm{J \cdot cm^{-3}}$)	s ($\mathrm{Å^{-1}}$)
Cyclopentane	94.815	1.347	1326.2	1.315	523	0.98 [7]
Cyclohexane	108.753	1.220	1132.7	1.291	535	0.93 [17]
Benzene	89.420	1.213	966.8	1.290	622	1.00 [15]
1,3-Dioxolane	69.965	1.164	765.6	1.280	743	1.23[a]

[a] Calculated from the method of Bondi [18].

Table VI. Contributions to Equimolecular V^E at 298.15 K According to PFP Theory Along with the Interaction Parameter, X_{12}, and Theoretical and Experimental V^E Values

System	H^E (J · mol^{-1})	X_{12} (J · cm^{-3})	ΔV_{int}^{a}	ΔV_{fv}^{a}	$\Delta V_{P^*}^*$^{a}	V^E_{th}^{a}	V^E_{expt}^{a}
$C_5H_{10}+C_3H_6O_2$	1562 [19]	84.21	1.157	−0.029	−0.194	0.934	0.609
$C_6H_{12}+C_3H_6O_2$	1581 [20]	77.11	1.111	−0.003	−0.061	1.047	0.926
$C_6H_6+C_3H_6O_2$	69.6 [21]	3.87	0.045	−0.002	−0.027	0.016	−0.099

^{a} (cm^3 · mol^{-1}).

pressure contributions are negative. The magnitude and sign of both contributions are dependent on the thermal expansion coefficients of the components. When these coefficients are similar, the mentioned contributions are small, and for these mixtures, they have little significance compared with the interaction contribution. The theoretical V^E values are in reasonable agreement with the experimental results. For the benzene + 1,3-dioxolane mixture the interaction contribution is positive but small, while the free volume and internal pressure contributions are negative and small due to the similar thermal expansion coefficients of the components. Both the calculated and the experimental V^E are small, but they have opposite signs. This difference can be attributed to the existence of specific interactions between benzene and 1,3-dioxolane.

4.2. Bloomfield–Dewan Theory

Several definitions have been used for the excess viscosity, but in order to apply the Bloomfield–Dewan theory, the most appropiate is

$$\Delta \ln \eta_{exp} = \ln \eta - (x_1 \ln \eta_1 + x_2 \ln \eta_2) \tag{6}$$

According to the Bloomfield–Dewan theory [22], the theoretical excess viscosity $\Delta \ln \eta_{th}$ is

$$\Delta \ln \eta_{th} = -\frac{\Delta H_M}{RT} + \frac{\Delta S^R}{R} + \left(\frac{1}{\tilde{V}-1} - \frac{x_1}{\tilde{V}_1 - 1} - \frac{x_2}{\tilde{V}_2 - 1}\right) \tag{7}$$

This equation displays explicitly the various contributions to the excess viscosities: the enthalpy of mixing, $\ln \eta_H$, the residual entropy of mixing, $\ln \eta_S$, and the free volume contribution, $\ln \eta_{fv}$. Reduced volumes of the mixture, $\tilde{V}$, and of the pure components, $\tilde{V}_1$ and $\tilde{V}_2$, the enthalpy of mixing, ΔH_M, and the residual entropy of mixing, ΔS^R, are calculated using

Table VII. Contributions to Equimolecular $\Delta \ln \eta$ at 298.15 K According to BD Theory Along with Theoretical and Experimental $\Delta \ln \eta$ Values

System	$\ln \eta_H$	$\ln \eta_S$	$\ln \eta_{fv}$	$\Delta \ln \eta_{th}$	$\Delta \ln \eta_{expt}$
$C_5H_{10} + C_3H_6O_2$	−0.527	0.141	−0.171	−0.557	−0.100
$C_6H_{12} + C_3H_6O_2$	−0.496	0.131	−0.155	−0.520	−0.128
$C_6H_6 + C_3H_6O_2$	−0.024	0.006	−0.010	−0.028	0.007

the Flory theory. Table VII shows the contributions to the equimolecular excess viscosity, together with the theoretical and experimental excess viscosities.

From a study of this table, it is observed that for mixtures containing a cycloalkane, $\ln \eta_H$ is negative and is the dominant term, and $\ln \eta_S$ and $\ln \eta_V$ have opposite signs and tend to cancel each other with $\ln \eta_S$ positive. The agreement between experimental and theoretical values is not very good, but the BD theory predicts the sign correctly. For the benzene + 1,3-dioxolane mixture, the different contributions have the same signs as those for the mixtures with cycloalkanes but their absolute values are very small. The calculated $\Delta \ln \eta$ values for this mixture are less satisfactory.

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