Relative Permittivities, Refractive Indices, and Densities of Dihydrofuran-2(3*H*)-one + Butan-1-ol and + Butan-2-ol at T = (293.15, 298.15, 303.15, and 313.15) K

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The experimental densities, ρ, relative permittivities, ε, and refractive indices, n_D, of binary mixtures of dihydrofuran-2(3*H*)-one + butan-1-ol and + butan-2-ol have been measured at T = (293.15 to 313.15) K and atmospheric pressure over the whole mole fraction range. From density data, excess molar volumes, V^E, were calculated at various temperatures. V^E is negative for all systems investigated. The experimental results have been correlated using the Redlich−Kister polynomial equation, and parameters from least-squares analysis have been reported.

Introduction

The physicochemical properties of liquid mixtures have attracted much attention from both theoretical and engineering application points of view. Dihydrofuran-2(3*H*)-one has important industrial applications and liquid−liquid extraction processes and is used as a stain remover, as superglue remover, as a paint stripper, as solvent in lithium batteries, in coating industries, and as an intermediate in different syntheses.[1−4] Understanding the mixing behavior of dihydrofuran-2(3*H*)-one with alkanols is therefore important and has applications in many engineering industries. Many engineering applications require quantitative data of liquid mixtures. It also provides information about the nature and molecular interactions between liquid mixture components.

This work continues our systematic studies of liquid−liquid extraction and the thermodynamic properties of mixtures containing dihydrofuran-2(3*H*)-one as one component.[4−6] A survey of the literature shows that the densities, viscosities, refractive indices, and relative permittivities of binary mixtures of dihydrofuran-2(3*H*)-one with *n*-alkanols and aromatic hydrocarbons have been reported at different temperatures.[7−10]

To examine the effect of branching in alkanols on mixing properties of mixtures of dihydrofuran-2(3*H*)-one and butanols, we report in the present paper the density ρ, excess molar volumes V^E, relative permittivity ε, and refractive index n_D for the binary mixtures of {dihydrofuran-2(3*H*)-one (1) + butan-1-ol (2) and + butan-2-ol (2)} over the whole mole fraction range at T = (293.15 to 313.15) K.

Experimental Section

Materials. Butan-1-ol (0.998 mass fraction purity) and butan-2-ol (0.995 mass fraction purity) were obtained from Aldrich and dihydrofuran-2(3*H*)-one (0.99 mass fraction purity) from Fluka AG and used without further purification. All liquids were kept over activated molecular sieves of type 4A (Union Carbide) and filtered before use. The purity of liquids was confirmed by gas−liquid chromatographic analysis. The measured density, refractive index, and relative permittivity data of the pure liquids at T = (293.15 to 313.15) K are shown in Table 1 together with literature data.

Table 1. Experimental Values of Density, ρ, Refractive Index, n_D, and Relative Permittivity, ε, for Pure Components at T = (293.15 to 313.15) K

		ρ/g·cm^{-3}		ε		n_D	
liquid	T/K	exptl	lit.	exptl	lit.	exptl	lit.
butan-1-ol	293.15	0.80952	0.8095[f]	18.26	18.28[e]	1.3992	1.3994[f]
	298.15	0.80558	0.80548[a]	17.54	17.54[e]	1.3972	1.3973[b]
	303.15	0.80192	0.8022[b]	16.89	16.91[e]	1.3963	1.3965[b]
	313.15	0.79426	0.7941[f]	15.45		1.3920	1.3909[f]
butan-2-ol	293.15	0.80554	0.8067[f]	17.51	17.51[e]	1.3971	1.3977[f]
	298.15	0.80206	0.80206[a]	16.58	16.60[e]	1.3954	1.3953[e]
	303.15	0.79845	0.7984[f]	15.75	15.75[e]	1.3928	1.39288[f]
	313.15	0.79007	0.7895[f]	14.44		1.3890	1.38818[f]
hydrofuran-2 (3*H*)-one	293.15	1.12879	1.1288[c]	42.81	42.35[c]	1.4370	1.4374[c]
	298.15	1.12375	1.1239[c]	41.64	41.68[c]	1.4356	1.4358[c]
	303.15	1.11879	1.1188[c]	41.1	41.06[c]	1.4334	1.4336[c]
	313.15	1.10888	1.10788[d]	39.92	39.91[g]	1.4290	1.42903[g]

[a] Rodriguez et al.[13] [b] Chmielewska et al.[12] [c] Martinez et al.[11] [d] Ritzoulis et al.[7] [e] Avraam et al.[9] [f] Yang et al.[8] [g] Fornefeld-Schwarz et al.[14]

Measurements. The densities of the pure component liquids and their binary mixtures were measured with a high-precision vibrating-tube digital densimeter (model DMA 60/602) whose measurement cell temperature was controlled automatically within ± 0.01 K of the selected value. Before each series of measurements, the densimeter was calibrated at atmospheric pressure with double distilled water and dry air. Densities, both water and dry air, at the various working temperatures were given by the manufacturer in the instruction manual. The uncertainty in the density measurements was within ± 3·10^{-5} g·cm^{-3}.

Relative permittivities were measured at 1 MHz with a Wissenschaftlich Technische Werkstätten GmbH, NF-Dekameter model DK 05. The measuring cell was NFL-2 and calibrated with standard liquids cyclohexane and dichloroethane. The

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10.1021/je900503p CCC: $40.75
Published on Web 11/06/2009

Table 2. Experimental Density, ρ, for {Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2) and + Butan-2-ol (2)} at T = (293.15 to 313.15) K

	ρ/g·cm^{-3}			
	T/K			
x_1	293.15	298.15	303.15	313.15
	Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2)			
0.0786	0.83112	0.82722	0.82357	0.81682
0.1555	0.85282	0.84894	0.84528	0.83930
0.2466	0.87928	0.87532	0.87163	0.86662
0.2901	0.89218	0.88819	0.88443	0.87994
0.3664	0.91523	0.91120	0.90736	0.90364
0.4332	0.93589	0.93177	0.92787	0.92487
0.4988	0.95654	0.95235	0.94838	0.94617
0.5616	0.97671	0.97246	0.96843	0.96689
0.6336	1.00034	0.99603	0.99192	0.99110
0.7033	1.02373	1.01935	1.01509	1.01508
0.7956	1.05539	1.05092	1.04655	1.04744
0.8654	1.08009	1.07534	1.07081	1.07254
0.9334	1.10436	1.09962	1.09488	1.09732
0.9888	1.12469	1.11977	1.11492	1.11810
	Hydrofuran-2(3*H*)-one (1) + Butan-2-ol (2)			
0.0564	0.82099	0.81752	0.81400	0.80557
0.1213	0.83911	0.83559	0.83199	0.82345
0.2541	0.87755	0.8739	0.87015	0.86153
0.3003	0.89134	0.88763	0.88383	0.87520
0.3895	0.91862	0.9148	0.91088	0.90214
0.4574	0.93995	0.93603	0.93202	0.92319
0.5005	0.95371	0.94973	0.94567	0.93683
0.5876	0.98213	0.97807	0.9739	0.96491
0.6442	1.00111	0.99691	0.99268	0.98359
0.7127	1.02455	1.02025	1.01592	1.00675
0.8006	1.05541	1.05096	1.04652	1.03712
0.8554	1.07508	1.07055	1.06603	1.05644
0.9262	1.10109	1.09644	1.09183	1.08197
0.9785	1.12058	1.11589	1.11121	1.10140

uncertainty in the values of the relative permittivity was estimated at ± 0.03.

Refractive index measurements were carried out with an Abbé refractometer (Tefsa, Germany), and the values here are the mean values from at least three independent readings for each solvent composition. The uncertainty in refractive index was better than ± 0.0002.

In all measurements, a Schott-Geräte CT1150 thermostat was used at a constant digital temperature control of ± 0.01 K.

Binary mixtures were prepared by mixing known masses of pure liquids in airtight-stoppered bottles to minimize the evaporation losses. All measurements of mass were performed on a Mettler balance (model AE-240) with a precision of ± 0.01 mg. The uncertainty in the mole fractions of the mixtures was estimated to be lower than ± $2 \cdot 10^{-4}$.

Results and Discussion

The experimental values of density ρ for {dihydrofuran-2(3*H*)-one (1) + butan-1-ol (2) and + butan-2-ol (2)} mixtures at T = (293.15 to 313.15) K over the whole mole fraction range are listed in Table 2. The excess molar volumes V^E for these binary mixtures were obtained from the following relation

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \qquad (1)$$

where x_1 and x_2 are the mole fractions; M_1 and M_2 are molar masses; ρ_1 and ρ_2 are the densities of the pure component liquids 1 and 2, respectively. ρ is the density of the binary mixtures. The calculated V^E data for {dihydrofuran-2(3*H*)-one (1) + butan-1-ol (2) and + butan-2-ol (2)} at T = (293.15 to 313.15) K are shown in Figures 1 and 2.

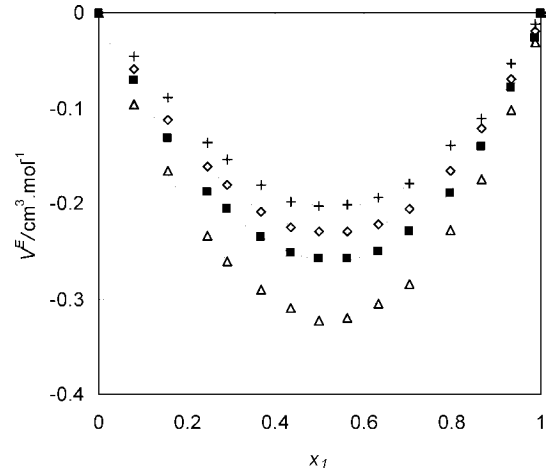

Figure 1. Excess molar volumes against mole fraction of {hydrofuran-2(3*H*)-one (1) + butan-1-ol (2)} at +, 293.15 K; ◇, 298.15 K; ■, 303.15 K; △, 313.15 K.

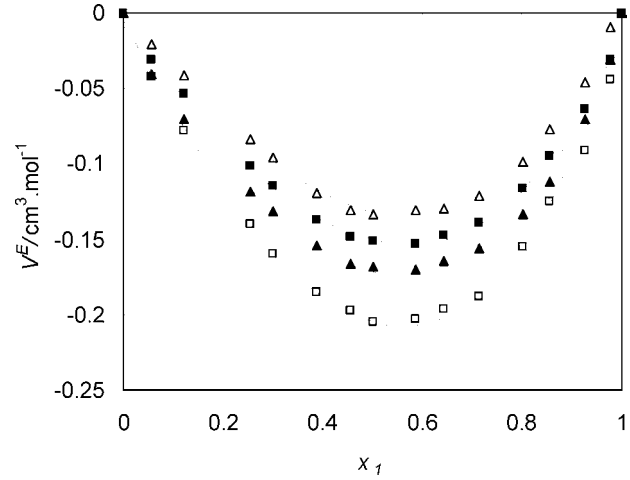

Figure 2. Excess molar volumes against mole fraction of {hydrofuran-2(3*H*)-one (1) + butan-2-ol (2)} at Δ, 293.15 K; ■, 298.15 K; ▲, 303.15 K; □, 313.15 K.

The values of V^E for each mixture were fitted to the Redlich−Kister polynomial equation.[15]

$$V^E = x_1x_2\sum_{i=0}^{n} A_i(x_1 - x_2)^i \qquad (2)$$

where A_i are adjustable parameters.

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of the standard deviation σ (V^E):

$$\sigma V = [\sum (V_{exptl} - V_{calcd})^2/(n - m)]^{1/2} \qquad (3)$$

where n is the total number of experimental points and m is the number of parameters. The fitting coefficients and the standard deviation values $\sigma(V^E)$ for binary mixtures of {dihydrofuran-2(3*H*)-one (1) + butan-1-ol (2) + butan-2-ol (2)} are given in Table 3.

It can be observed from the experimental results in Figures 1 and 2 that V^E values are negative over the whole mole fraction range at T = (293.15 to 313.15) K for the binary mixtures of {dihydrofuran-2(3*H*)-one (1) + butan-1-ol (2) and + butan-2-ol (2)}. The negative V^E values indicate that there is a volume contraction on mixing. Such behavior is a result of several opposing effects: dipolar−dipolar interactions between dihy-

Table 3. Coefficients, A_i, of the Redlich−Kister Equation for {Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2) and + Butan-2-ol (2)} at T = (293.15 to 313.15) K

	T/K	A_0	A_1	A_2	A_3	σ
	Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2)					
V^E/cm^3·mol^{-1}	293.15	−0.8171	−0.1175	0.1048	−0.0282	0.0041
	298.15	−0.8922	0.1095	−0.2081	−0.6049	0.0032
	303.15	−1.0373	−0.1434	−0.1223		0.0033
	313.15	−1.2691	−0.1533	−0.2641		0.0038
	Hydrofuran-2(3*H*)-one (1) + 2-Butanol (2)					
	293.15	−0.525	−0.1516	0.0028	−0.0104	0.0038
	298.15	−0.5877	−0.1369	−0.1791	−0.0911	0.0040
	303.15	−0.5781	0.2177	−0.7725	−0.0092	0.0030
	313.15	−0.7086	−0.261	−0.7555	−1.0332	0.0022

Table 4. Experimental Values of Refractive Index, n_D, for {Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2) and + Butan-2-ol (2)} at T = (293.15 to 313.15) K

	n_D			
	T/K			
x_1	293.15	298.15	303.15	313.15
	Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2)			
0.1098	1.4026	1.4014	1.4000	1.3973
0.2154	1.4063	1.4051	1.4038	1.4013
0.3009	1.4096	1.4083	1.4070	1.4044
0.4127	1.4136	1.4124	1.4111	1.4085
0.5088	1.4172	1.4160	1.4147	1.4121
0.6124	1.4213	1.4200	1.4186	1.4158
0.7001	1.4247	1.4234	1.4219	1.4192
0.8133	1.4294	1.4279	1.4263	1.4232
0.9078	1.4332	1.4316	1.4300	1.4267
	Hydrofuran-2(3*H*)-one (1) + Butan-2-ol (2)			
0.1009	1.3992	1.3971	1.3948	1.3910
0.2112	1.4011	1.3992	1.3974	1.3936
0.3009	1.4022	1.4001	1.3981	1.3942
0.4008	1.4045	1.4014	1.3988	1.3945
0.5088	1.4078	1.4047	1.4018	1.3961
0.6003	1.4112	1.4072	1.4031	1.3987
0.7001	1.4152	1.4121	1.4092	1.4023
0.8055	1.4216	1.4178	1.4142	1.4082
0.9011	1.4285	1.4256	1.4228	1.4173

drofuran-2(3*H*)-one molecules and butanols, hydrogen bond breaking in butanol structures, a new hydrogen bond formation between −*C*−*O* groups in dihydrofuran-2(3*H*)-one with hydroxyl groups −OH in butanols, and changes of free volume in the real mixtures. The less negative V^E values for butan-2-ol mixtures serve as evidence that the interactions between dihydrofuran-2(3*H*)-one and butan-2-ol are weaker than those between the butan-1-ol and dihydrofuran-2(3*H*)-one. Such behavior may be due to the steric hindrance of the methyl group $-CH_3$ in butan-2-ol. The negative V^E values at equimolar concentrations of the binary mixtures follow the order: butan-1-ol > butan-2-ol. We found a reasonable agreement between our experimental V^E results for dihydrofuran-2(3*H*)-one (1) + butan-1-ol (2) at 298.15 K and x_1 = 0.5 (−0.2231) and those reported by Ritzoulis et al.[7] (−0.2225).

The measured values for the refractive index, n_D, of the binary mixtures of dihydrofuran-2(3*H*)-one + butan-1-ol (2) and + butan-2-ol (2) over the whole mole fraction range and T = (293.15 to 313.15) K are given in Table 4. The refractive indices of the mixtures as a function of the mole fraction at 298.15 K are shown in Figure 3. The experimental values of the relative permittivity, ε, of the investigated mixtures over the whole mole fraction and T = (293.15 to 313.15) K are listed in Table 5. The relative permittivities of the mixtures as a function of the mole fraction at 298.15 K are shown in Figure 4. The overall appearance of the curves of refractive indices and relative permittivities does not

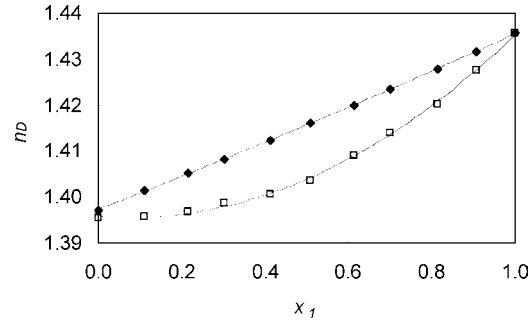

Figure 3. Variation of the refractive index, n_D, with the mole fraction of hydrofuran-2(3*H*)-one at 298.15 K. ◆, hydrofuran-2(3*H*)-one (1) + butan-1-ol (2); □, hydrofuran-2(3*H*)-one (1) + butan-2-ol (2).

Table 5. Experimental Values of Relative Permittivity, ε, for {Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2) and + Butan-2-ol (2)} at T = (293.15 to 313.15) K

	ε			
	T/K			
x_1	293.15	298.15	303.15	313.15
	Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2)			
0.1098	19.41	18.96	18.57	17.28
0.2154	20.78	20.23	19.99	19.49
0.3009	21.88	21.71	21.61	21.26
0.4127	24.22	24.05	23.88	23.51
0.5088	26.44	26.16	26.16	25.65
0.6124	29.19	28.86	28.82	28.05
0.7001	31.79	31.36	31.34	30.46
0.8133	35.88	35.12	35.03	33.79
0.9078	39.34	38.55	38.46	36.94
	Hydrofuran-2(3*H*)-one (1) + Butan-2-ol (2)			
0.1009	17.91	17.43	16.75	16.09
0.2112	19.08	18.75	18.21	17.48
0.3009	20.56	19.99	19.37	18.55
0.4008	22.53	21.88	21.28	20.43
0.5088	25.16	24.31	23.71	22.86
0.6003	27.69	26.79	26.26	25.55
0.7001	30.91	29.97	29.48	28.79
0.8055	34.66	33.72	33.39	32.73
0.9011	38.29	37.47	37.37	36.45

change with temperature. The experimental refractive indices and relative permittivities of the investigated binary mixtures at all temperatures studied were smoothed by the equation of the form

$$Y = \sum_{i=0} b_i x_1^i \qquad (4)$$

where Y is either n_D or ε. The adjustable parameters, b_i, were obtained by linear regression and are summarized in Table 6

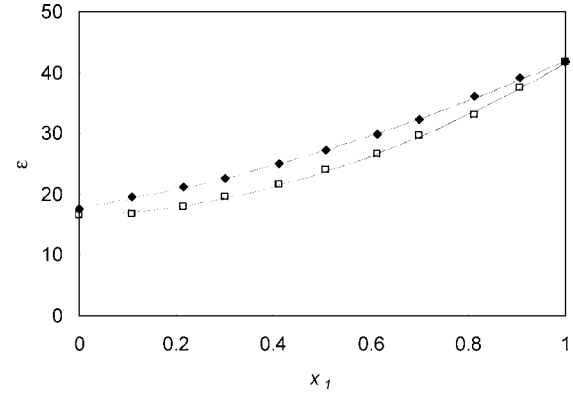

Figure 4. Variation of relative permittivity against mole fraction of hydrofuran-2(3*H*)-one at 298.15 K. ◆, hydrofuran-2(3*H*)-one (1) + butan-1-ol (2); □, hydrofuran-2(3*H*)-one (1) + butan-2-ol (2).

Table 6. Coefficients b_i and Standard Deviations σ for the Fit of the Refractive Index, n_D, and Relative Permittivity, ε, to Equation 4 at Temperature T and Atmospheric Pressure

property	T/K	b_0	b_1	b_2	σ
	Hydrofuran-2(3*H*)-one (1) + Butan-1-ol (2)				
n_D	293.15	1.399	0.0334	0.0046	0.0002
	298.15	1.3973	0.0353	0.0028	0.0004
	303.15	1.3962	0.0353	0.002	0.0002
	313.15	1.3924	0.0414	−0.0044	0.0005
ε	293.15	18.32	7.04	17.6	0.04
	298.15	17.84	9.37	14.84	0.03
	303.15	16.95	11.68	12.79	0.04
	313.15	15.61	15.17	9.09	0.04
	Hydrofuran-2(3*H*)-one (1) + Butan-2-ol (2)				
n_D	293.15	1.4	−0.007	0.0433	0.0002
	298.15	1.3981	−0.015	0.0507	0.0004
	303.15	1.3956	−0.0194	0.0542	0.0004
	313.15	1.3926	−0.0254	0.058	0.0005
ε	293.15	17.33	4.66	20.82	0.02
	298.15	16.67	4.99	20.01	0.04
	303.15	15.9	5.58	19.85	0.04
	313.15	14.79	7.22	18.24	0.04

along with the standard deviations σ, calculated by the expression

$$\sigma = \frac{1}{n-p}\sum_{n}(Y_{\text{exptl}} - Y_{\text{calcd}})^2 \qquad (5)$$

where Y_{exptl} and Y_{calcd} are the experimental data and calculated values, respectively; n is the number of experimental points; and p is the number of coefficients.

Conclusion

This paper reports new experimental data for the densities, refractive indices, and relative permittivities for the binary mixtures of {hydrofuran-2(3*H*)-one (1) + butan-1-ol (2), + butan-2-ol (2)} which were measured at temperatures from T = (293.15 to 313.15) K and at atmospheric pressure over the whole mole fraction range. The excess molar volumes, V^E, for these binary mixtures determined from the experimental density measurements were fitted to the Redlich−Kister polynomial equation. V^E values are negative for the binary mixtures of {hydrofuran-2(3*H*)-one (1) + butan-1-ol (2) and + butan-2-ol (2)} over the whole mole fraction range and investigated temperatures. Such behavior may be a result of several opposing effects: dipolar−dipolar interactions, hydrogen bond breaking in butanols, hydrogen bond formation between the −CO of dihydrofuran-2(3*H*)-one and the −OH of butanols, and alkanol functional group (−OH) at an internal carbon.

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Received for review June 15, 2009. Accepted October 29, 2009. Financially supported by the The Institute of International Education. IIE is gratefully acknowledged.

JE900503P