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A Study on Excess Volumes and Dielectric Properties in the γ-Butyrolactone + *p*-Xylene System at Various Temperatures

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Densities, relative permittivities, and refractive indices were measured for the binary mixture γ-butyrolactone + *p*-xylene from 288.15 K to 308.15 K. The above quantities are represented with polynomial smoothing curves. Excess volumes, as well as deviations of molar polarization, were calculated and found to be negative, with a minimum at mole fraction 0.5. The Kirkwood correlation factor was also calculated.

Introduction

γ-Butyrolactone is one of the most interesting solvents in connection with lithium batteries and active metal electrochemistry. Considerable research has been done in the investigation of the properties and the electrochemical behavior of this solvent (Pistoia, 1994; Gabano, 1983; Aurbach, 1989; Aurbach and Chusid, 1994; Tobishima and Okada, 1985). Mixtures of γ-butyrolactone with other organic solvents are also of interest (Awwad et al., 1988; Ramkumar and Kudchadker, 1989).

In this work, the density, relative permittivity, and refractive index for the binary system γ-butyrolactone + *p*-xylene over the whole composition range from 288.15 K to 308.15 K were measured. From these results the excess volume, molar polarization and Kirkwood correlation factor were derived.

Experimental Section

γ-Butyrolactone (Aldrich, >99%) was purified by being distilled twice under reduced pressure, as has been proposed (Aurbach and Gottlieb, 1989). *p*-Xylene (Fluka, puriss p.a. >99%) was also distilled, and the middle fraction was collected.

Density measurements were made with an Anton-Paar DMA 602/60 vibrating tube densimeter, which was thermostated by a Haake F3-K digital thermostat with a stability of ±0.02 K. The accuracy in density measurements was better than $\pm 5 \times 10^{-5}$ g cm^{-3} and in excess volume ±0.007 cm^3 mol^{-1}. Relative permittivities were measured with a Wissenschaftlich Technische Werkstätten GmbH, model DM-01, dipolmeter. The temperature of the dipolmeter was regulated by a YSI (model 72) thermostat with a stability of ±0.005 K. The uncertainty in ϵ was lower than 0.3%. Refractive index measurements were taken by means of an Abbe refractometer (aus JENA, model G), using sodium light (D). The refractometer was thermostated to ±0.005 K with the same thermostat mentioned in relative permittivity measurements. The error in refractive index was lower than ±0.0002 units.

All solutions were prepared by mass. The atomic masses were taken from the atomic mass table of IUPAC (IUPAC, 1996). Details for density, relative permittivity, and refractive index measurements are given elsewhere (Konti et al., 1997).

Results and Discussion

Density, relative permittivity, and refractive index experimental values are given in Table 1. The experimental values of the pure components are given in Table 2 and are compared with literature values. Our density values of γ-butyrolactone are in agreement with the values reported by Ramkumar and Kudchadker (1989). Pistoia reports the values 41.7 and 39.1 (Pistoia, 1994) for the relative permittivity of γ-butyrolactone at 298.15 K; the value found here is 41.68 and agrees with the first one.

Density and relative permittivity experimental data of *p*-xylene are also in agreement with the literature ones, as well as the refractive index data, where the difference between the experimental and the literature values is less than 0.01%.

The experimental data were fitted to the equation

$$Y = \sum_{j=0} a_j x_1^j \qquad (1)$$

to get smoothing values for relative permittivity and refractive index. In eq 1 x_1 is the mole fraction of γ-butyrolactone, a_j are the coefficients obtained by a regression analysis based on the least-squares method, and Y can represent the relative permittivity or the refractive index. The values of coefficients a_j and the standard deviations are given in Tables 3 and 4.

Excess volume, V^E, was calculated from density measurements from the equation

$$V^E = M_1 x_1\left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + M_2 x_2\left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \qquad (2)$$

where M_i, x_i, and ρ_i are, respectively, the molar mass, the mole fraction, and the density of the pure component, and ρ the density of the mixture. The V^E values were fitted

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Table 1. Density, ρ, Relative Permittivity, ϵ, and Refractive Index, n_D, Experimental Values for γ-Butyrolactone (1) + p-Xylene (2) Mixtures from 288.15 K to 308.15 K

x_1	ρ/(g cm^{-3})	ϵ	n_D
	288.15 K		
0.0000	0.8653	2.28	1.4981
0.1205	0.8882	4.47	1.4953
0.1787	0.9002	5.63	1.4930
0.2913	0.9242	8.44	1.4886
0.3991	0.9487	11.71	1.4837
0.5022	0.9742	15.50	1.4782
0.6012	1.0006	19.68	1.4719
0.6961	1.0283	24.33	1.4658
0.7872	1.0572	29.27	1.4588
0.9173	1.1009	37.35	1.4476
1.0000	1.1333	43.07	1.4392
	293.15 K		
0.0000	0.8612	2.27	1.4958
0.1205	0.8842	4.38	1.4929
0.1787	0.8960	5.54	1.4909
0.2913	0.9200	8.34	1.4862
0.3991	0.9445	11.58	1.4813
0.5022	0.9699	15.22	1.4763
0.6012	0.9963	19.36	1.4702
0.6961	1.0240	23.90	1.4639
0.7872	1.0528	28.70	1.4570
0.9173	1.0967	36.80	1.4455
1.0000	1.1288	42.35	1.4374
	298.15 K		
0.0000	0.8566	2.26	1.4931
0.1205	0.8796	4.33	1.4903
0.1787	0.8914	5.47	1.4884
0.2913	0.9153	8.23	1.4839
0.3991	0.9398	11.40	1.4791
0.5022	0.9652	15.01	1.4740
0.6012	0.9915	19.06	1.4681
0.6961	1.0191	23.55	1.4619
0.7872	1.0479	28.24	1.4551
0.9173	1.0916	36.17	1.4439
1.0000	1.1239	41.68	1.4358
	303.15 K		
0.0000	0.8521	2.25	1.4904
0.1205	0.8751	4.31	1.4880
0.1787	0.8869	5.42	1.4857
0.2913	0.9107	8.08	1.4814
0.3991	0.9350	11.20	1.4766
0.5022	0.9604	14.76	1.4716
0.6012	0.9868	18.75	1.4659
0.6961	1.0143	23.18	1.4596
0.7872	1.0431	27.85	1.4529
0.9173	1.0869	35.66	1.4421
1.0000	1.1188	41.06	1.4336
	308.15 K		
0.0000	0.8478	2.24	1.4878
0.1205	0.8707	4.26	1.4852
0.1787	0.8825	5.37	1.4832
0.2913	0.9063	7.94	1.4790
0.3991	0.9305	11.07	1.4743
0.5022	0.9558	14.58	1.4694
0.6012	0.9820	18.44	1.4634
0.6961	1.0094	22.75	1.4570
0.7872	1.0382	27.4	1.4503
0.9173	1.0818	35.11	1.4399
1.0000	1.1135	40.48	1.4316

Table 2. Experimental and Literature Values of the Pure Liquids for Density, Relative Permittivity, and Refractive Index

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
			γ-Butyrolactone		
ρ/g cm^{-3}	1.1333[a] 1.1336[b]	1.1288[a] 1.1280[b]	1.1239[a] 1.1237[b]	1.1188[a] 1.1189[b]	1.1135[a]
ϵ	43.07[a]	42.35[a]	41.68[a] 41.7[c] 39.1[c]	41.06[a]	40.48[a]
n_D	1.4392[a]	1.4374[a]	1.4358[a]	1.4336[a]	1.4316[a]
			p-Xylene		
ρ/g cm^{-3}	0.8653[a] 0.86488[d]	0.8612[a] 0.86073[d]	0.8566[a] 0.85672[d] 0.85673[e] 0.8566[f] 0.85661[g]	0.8521[a] 0.85239[d] 0.8523[f]	0.8478[a] 0.84782[e] 0.8479[f]
ϵ	2.28[a]	2.27[a]	2.26[a] 2.2618[e]	2.25[a]	2.24[a] 2.2447[e]
n_D	1.4981[a]	1.4958[a]	1.4931[a] 1.49323[d] 1.49312[e] 1.4932[h]	1.4904[a] 1.4905[i]	1.4878[a] 1.4877[e]

[a] This work. [b] Ramkumar and Kudchadker, 1989. [c] Pistoia, 1994. [d] Serrano et al., 1990. [e] Buep and Barón, 1988. [f] Tasioula-Margari and Demetropoulos, 1992. [g] Awwad et al., 1988. [h] Nath and Narain, 1982. [i] Rao and Viswanath, 1982.

Table 3. Coefficients a_j and Standard Deviations σ of Eq 1 for the Relative Permittivity Representation of the γ-Butyrolactone (1) + p-Xylene (2) System

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
a_0	2.28	2.27	2.26	2.25	2.24
a_1	16.53	15.40	14.87	15.04	14.55
a_2	7.90	15.19	16.36	13.00	14.59
a_3	33.92	12.65	10.11	15.64	11.47
a_4	−26.19	−3.12	−1.91	−4.83	−2.36
a_5	8.65				
σ	0.024	0.049	0.042	0.035	0.041

Table 4. Coefficients a_j and Standard Deviations σ of Eq 1 for the Refractive Index Representation of the γ-Butyrolactone (1) + p-Xylene (2) System

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
a_0	1.4981	1.4958	1.4931	1.4904	1.4878
a_1	−0.0189	−0.0212	−0.0191	−0.0166	−0.0180
a_2	−0.0559	−0.0448	−0.0490	−0.0608	−0.0460
a_3	0.0399	0.0260	0.0315	0.0524	0.0220
a_4	−0.024	−0.0186	−0.0208	−0.0318	−0.0141
$10^4\sigma$	1.28	1.53	0.96	1.63	1.77

Table 5. Coefficients b_j and Standard Deviations σ of Eq 3 for the γ-Butyrolactone (1) + p-Xylene (2) System

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
b_0	−2.316	−2.375	−2.400	−2.431	−2.476
b_1	0.059	0.032	0.072	0.024	0.034
b_2	−2.192	−1.909	−1.958	−2.013	−2.033
b_3	0.403	0.393	0.584	0.524	0.434
b_4	4.109	3.234	3.542	3.166	3.112
σ/cm^3 mol^{-1}	0.051	0.052	0.057	0.047	0.059

through least-squares to a Redlich−Kister (Redlich and Kister, 1948) type equation

$$V^E = x_1 x_2 \sum_{j=0} b_j (x_1 - x_2)^j \tag{3}$$

Coefficients b_j and standard deviations are given in Table 5. Variations of V^E with the mole fraction of γ-butyrolactone are represented in Figure 1. Excess volumes are negative in all of the composition range, showing a minimum at $x_1 = 0.5$, at the five temperatures. On increasing the temperature, the deviation from the ideal behavior increases. This has been observed many times (Konti et al., 1997; Jannelli et al., 1983; Lopez et al., 1983; Moumouzias et al., 1991; Moumouzias and Ritzoulis, 1992).

The relative permittivity results were used to deduce the molecular association through the specific dipole interactions. Kirkwood (Kirkwood, 1939; Böttcher, 1973) introduced a correlation factor, g, to clarify the role of the existence of intermolecular interactions; it is a measure of

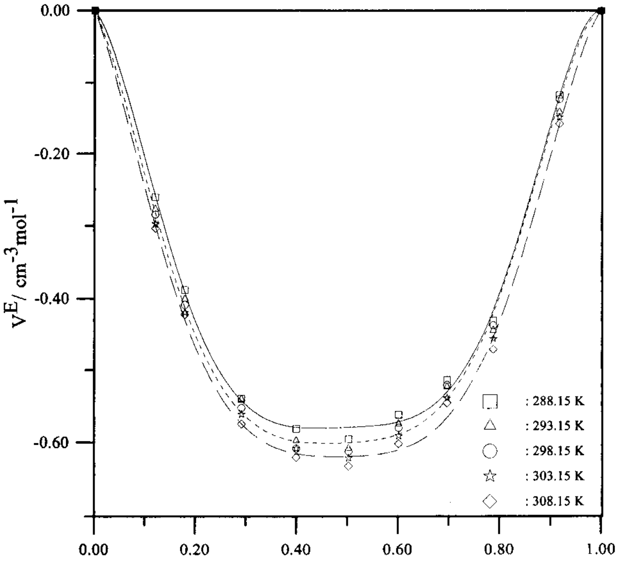

Figure 1. Variation of excess volume, V^E, with the mole fraction of γ-butyrolactone, x_1. Curves are least-squares representations by eq 3 (—, 288.15 K; ···, 298.15 K, - - -, 308.15 K).

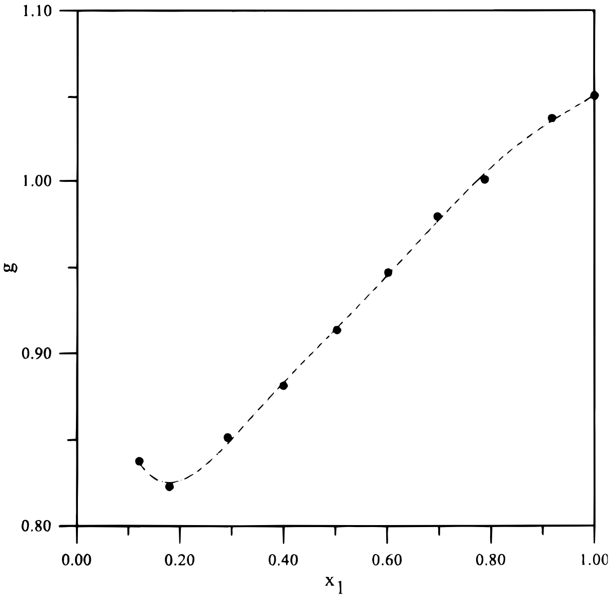

Figure 2. Variation of Kirkwood correlation factor, g, with the mole fraction of γ-butyrolactone, x_1, at 298.15 K. Curve shows the general trend.

the short-range forces that orient the dipole–dipole moments.

The equation proposed by Fröhlich for the calculation of dipole moments of polar solutes in nonpolar solvents is (Böttcher, 1973)

$$g\mu_0^2 = \frac{9kT(2\epsilon + \epsilon_\infty)^2}{4\pi N_A x_1(\epsilon_\infty + 2)^2(2\epsilon + 1)} \times \left[\frac{V(\epsilon - 1)}{\epsilon} - \frac{3(1 - x_1)V_2(\epsilon_2 - 1)}{(2\epsilon + \epsilon_2)} - \frac{3x_1V_1(\epsilon_\infty - 1)}{(2\epsilon + \epsilon_\infty)}\right] \quad (4)$$

where μ_0 is the dipole moment of the isolated polar molecule taken from literature, 4.19 D (Wallmark et al., 1970), k and N_A are Boltzmann's constant and Avogadro's number, respectively, T is the temperature in kelvin, ϵ and ϵ_2 are the relative permittivity of the mixture and the nonpolar component, and ϵ_∞ is the high-frequency relative permittivity, characteristic of induced polarization for pure polar solute. ϵ_∞ was taken equal to the square of the refractive index, n_D, as is the most common expression (Barthel and Feuerlein, 1986; Stokes and Marsh, 1976; Swain and Ray, 1985). x_1 is the mole fraction of the polar solute, V_1 and V_2 are the molar volume of the polar and the nonpolar component respectively, and V the molar volume of the mixture, defined by $V = (x_1M_1 + x_2M_2)/\rho$.

Table 6. Calculated Values of Molar Polarization P_m (cm^{-3} mol^{-1}) for the γ-Butyrolactone (1) + p-Xylene (2) System

x_1	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
0.0000	1.45	1.33	1.26	1.19	1.10
0.1205	72.49	70.37	69.46	69.40	68.47
0.1787	103.17	101.32	100.08	99.39	98.66
0.2913	169.84	168.25	166.46	163.64	161.00
0.3991	239.18	237.30	234.33	230.89	229.02
0.5022	312.40	307.63	304.56	300.54	298.04
0.6012	386.14	381.11	376.67	371.96	367.21
0.6961	461.43	454.81	450.01	444.69	438.18
0.7872	534.30	525.65	519.37	514.29	508.07
0.9173	641.99	634.68	626.44	620.05	613.11
1.0000	708.74	699.39	691.04	683.64	676.99

Table 7. Coefficients c_j and Standard Deviations σ of Eq 7 for the γ-Butyrolactone (1) + p-Xylene (2) System

	288.15 K	293.15 K	298.15 K	303.15 K	308.15 K
c_0	−177.06	−172.36	−169.17	−171.25	−170.39
c_1	50.9	29.24	32.6	38.53	29.55
c_2	22.59	−7.63	−3.3	7.17	−14.59
c_3	−71.75	−16.99	−28.65	−43.43	−40.86
c_4	105.62	143.94	123.45	131.9	152.13
σ/cm^3 mol^{-1}	2.4	3.5	3.6	2.6	1.4

For pure γ-butyrolactone the correlation parameter, g, is close to unity, which means that there is no correlation between the orientations of neighboring molecules. According to the Kirkwood–Fröhlich theory for systems in which the specific intermolecular forces cause alignment of neighboring dipoles in a parallel fashion, g is greater than unity, whereas for antiparallel alignment g values are less than unity.

The calculated values of the Kirkwood correlation factor at 298.15 K for the mixture γ-butyrolactone + p-xylene are represented graphically in Figure 2. g is less than unity almost throughout the mole fraction range, meaning that the dipole moments of the complex species that are formed have an orientation in an antiparallel fashion.

Molar polarization of the mixture, P_m, was calculated from the equation

$$P_m = \frac{(\epsilon - n_D^2)(2\epsilon + n_D^2)}{9\epsilon} V \quad (5)$$

and the deviation of the molar polarization, ΔP_m, was calculated from

$$\Delta P_m = P_m - (x_1P_{m,1} + x_2P_{m,2}) \quad (6)$$

where $P_{m,i}$ refers to the pure component. The calculated values of P_m are given in Table 6. The obtained ΔP_m values were fitted to the equation

$$\Delta P_m = x_1x_2\sum_{j=0} c_j(x_1 - x_2)^j \quad (7)$$

Equation 7 has also been used by others (Ruostesuo and Liias-Lepisto, 1991). The values of coefficients c_j and the standard deviations are listed in Table 7. Variation of ΔP_m

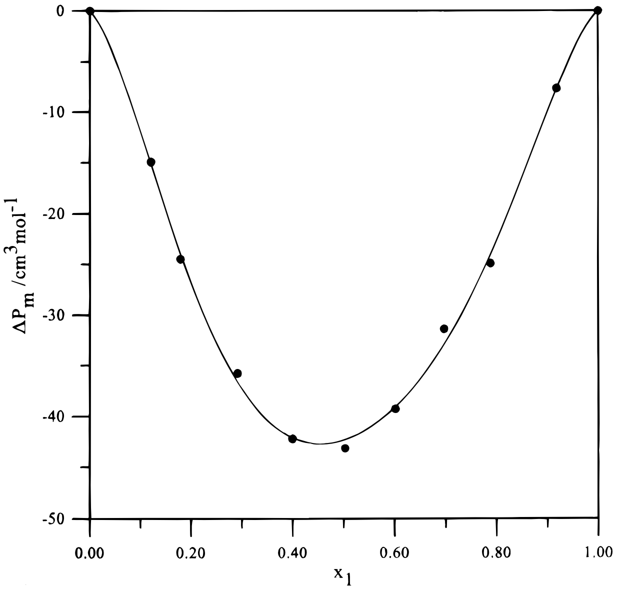

Figure 3. Variation of ΔP_m, with the mole fraction of γ-butyrolactone, x_1, at 298.15 K. Curve is the least-squares representation by eq 7.

with the mole fraction of γ-butyrolactone, at 298.15 K, is represented in Figure 3. ΔP_m is negative in all of the composition range, with a minimum at $x_1 = 0.5$. The influence of temperature on ΔP_m was found to be insignificant.

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