J. Chem. Eng. Data **2005,** *50,* 261−263

Densities and Viscosities of Binary Mixtures of Paraldehyde + Propylene Carbonate at (288.15, 293.15, 298.15, 303.15, and 308.15) K

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The densities and viscosities of binary mixtures of paraldehyde + propylene carbonate have been measured at (288.15, 293.15, 298.15, 303.15, and 308.15) K. From these measurements, excess molar volumes (V^E) and viscosity deviations ($\delta\eta$) were calculated. These results were fit to a Redlich−Kister polynomial. The results were discussed in terms of molecular interactions.

Introduction

Drug macromolecular interactions are important phenomena in physiological media such as blood, membranes, and intra- and extracellular fluids.[1] The use of paraldehyde as a liquid drug has caused increased interest in understanding the molecular interactions with the other solvents. Because the physiochemical parameters of the above-mentioned system do not exist in the literature, we have undertaken a study of the measurement of physical properties of the binary mixtures of paraldehyde with propylene carbonate. In the present work, we have systematically studied the excess properties of the binary mixtures of paraldehyde with propylene carbonate at various temperatures. We are reporting the excess molar volumes and viscosity deviations for binary mixtures of paraldehyde with propylene carbonate at different temperatures.

Experimental Section

Materials. Paraldehyde (Merck, ≥98%) was used as such without further purification. Propylene carbonate (Merck, ≥99%) was refluxed over anhydrous calcium carbonate and distilled at atmospheric pressure. The middle fraction collected was stored over 4Å molecular sieves.[2,3] Triply distilled propylene carbonate was used. The purity of purified propylene carbonate was checked by comparing the observed densities and viscosities with those reported in the literature.[3] The measured values are included in Table 1 along with the literature values. The experimental and literature values show good agreement.

Measurements. The densities of the pure components and their mixtures were measured using a single-arm capillary pycnometer having a bulb volume of approximately 5 cm^3 and a capillary bore with an internal diameter of 0.75 mm. The uncertainty in the density measurements was found to be $\pm 5 \times 10^{-5}$ g·cm^{-3}.

The volume (v) of the pycnometer up to the mark in the capillary was determined using triply distilled water at 288.15 K by taking the mass (m) of water and the literature density[4] at 288.15 K by using the relation $v = {}^{m}/_{\rho}$. The density for the next temperature at 293.15 K was determined by measuring an increase in the height of the water level from the mark with the help of a travelling microscope having at least a count of 0.001 cm. The increased volume (v_i) of water was calculated from equation $v_i = \pi r^2 h$, where h is the height of the increased water level and r is the radius of the capillary and is added to volume v at 288.15 K.

Table 1. Comparison of Experimental and Literature Values of Density, ρ, and Viscosity, η, for Pure Compounds

		ρ/g·cm^{-3}		η/mPa·s	
liquid	T/K	exptl	lit[a]	exptl	lit[a]
propylene carbonate	288.15	1.20867	1.2087	3.086	3.0860
	293.15	1.20338	1.2034	2.762	2.7635
	298.15	1.19758	1.1978	2.499	2.5009
	303.15	1.19253	1.1926	2.271	2.2743
	308.15	1.18716	1.1873	2.073	2.0797

[a] Moumouzias et al.[3]

The density of triply distilled water at 293.15 K was calculated using the relation $\rho = m/(v + v_i)$, where m is the mass at 288.15 K. The observed density (0.99821 g·cm^{-3}) was close to the literature value[4] (0.99826 g·cm^{-3}). The densities of the mixtures were determined by taking the mass at 288.15 K and using this mass and v_i at each temperature as described above. The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight stoppered bottles to minimize evaporation losses. All masses were measured on a Mettler one-pan balance (E-Mettler, Zurich), which can read up to five decimal places with an accuracy of ±0.05 mg. The uncertainty in the compositions (mole fractions) of the mixtures was estimated to be $\pm 5 \times 10^{-5}$ g.

Viscosity measurements were performed by using Schott Gerate (AVS 350) viscosity measuring equipment with a series of Ubbelhode viscometers. In all of the measurements, kinetic energy corrections have been taken into account. According to the method suggested by Hagenbach (AVS 350, viscosity-measuring system, Instruction Manual Schott Gerate Hofheim, IS Germany 1986), measurements were performed at least five times for each solution and at each temperature, and the results were averaged. The experimental repeatability of the viscosity measurements at each temperature for each solution was ±0.002 mPa.s. For all of the measurements, temperature was controlled by circulating water through an ultrathermostat JULABO F-25 (made in Germany), which has an accuracy of ±0.02 °C.

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10.1021/je0496903 CCC: $30.25

Table 2. Densities, ρ, Viscosities, η, Excess Molar Volumes, V^E, and Viscosity Deviations, $\delta\eta$, for the Binary Mixture Paraldehyde (1) + Propylene Carbonate (2) at (288.15, 293.15, 298.15, 303.15, and 308.15) K

x_1	ρ/g·cm^{-3}	η/mPa·s	V^E/cm^3·mol^{-1}	$\delta\eta$/mPa·s
		T = 288.15 K		
0.0000	1.20867	3.086	0.000	0.000
0.0910	1.18168	2.966	−0.099	0.035
0.2019	1.15181	2.809	−0.198	0.068
0.3007	1.12763	2.661	−0.265	0.089
0.4055	1.10407	2.494	−0.311	0.102
0.5011	1.08421	2.333	−0.328	0.105
0.6022	1.06471	2.155	−0.318	0.100
0.7006	1.04698	1.974	−0.278	0.087
0.8028	1.02973	1.779	−0.202	0.067
0.9028	1.01400	1.581	−0.106	0.040
1.0000	0.99969	1.374	0.000	0.000
		T = 293.15 K		
0.0000	1.20338	2.762	0.000	0.000
0.0910	1.17649	2.641	−0.112	0.019
0.2019	1.14669	2.499	−0.224	0.047
0.3007	1.12253	2.364	−0.299	0.065
0.4055	1.09895	2.215	−0.349	0.077
0.5011	1.07906	2.070	−0.367	0.079
0.6022	1.05949	1.910	−0.354	0.074
0.7006	1.04168	1.750	−0.307	0.065
0.8028	1.02434	1.577	−0.222	0.049
0.9028	1.00853	1.402	−0.118	0.028
1.0000	0.99414	1.224	0.000	0.000
		T = 298.15 K		
0.0000	1.19758	2.499	0.000	0.000
0.0910	1.17078	2.386	−0.122	0.013
0.2019	1.14110	2.245	−0.247	0.026
0.3007	1.11702	2.116	−0.332	0.035
0.4055	1.09350	1.977	−0.391	0.042
0.5011	1.07363	1.846	−0.413	0.044
0.6022	1.05405	1.705	−0.401	0.044
0.7006	1.03619	1.563	−0.350	0.039
0.8028	1.01875	1.412	−0.252	0.030
0.9028	1.00279	1.260	−0.127	0.018
1.0000	0.98835	1.107	0.000	0.000
		T = 303.15 K		
0.0000	1.19253	2.271	0.000	0.000
0.0910	1.16571	2.161	−0.132	0.005
0.2019	1.13599	2.027	−0.266	0.012
0.3007	1.11187	1.907	−0.357	0.018
0.4055	1.08830	1.779	−0.421	0.023
0.5011	1.06837	1.661	−0.445	0.026
0.6022	1.04871	1.531	−0.432	0.025
0.7006	1.03077	1.402	−0.377	0.021
0.8028	1.01322	1.268	−0.271	0.016
0.9028	0.99717	1.134	−0.137	0.009
1.0000	0.98264	1.001	0.000	0.000
		T = 308.15 K		
0.0000	1.18716	2.073	0.000	0.000
0.0910	1.16025	1.969	−0.138	0.002
0.2019	1.13048	1.843	−0.283	0.006
0.3007	1.10633	1.732	−0.384	0.009
0.4055	1.08274	1.614	−0.458	0.013
0.5011	1.06277	1.505	−0.489	0.016
0.6022	1.04305	1.385	−0.478	0.014
0.7006	1.02500	1.267	−0.419	0.011
0.8028	1.00731	1.144	−0.302	0.007
0.9028	0.99106	1.024	−0.147	0.004
1.0000	0.97644	0.907	0.000	0.000

Table 3. Values of the Coefficients of the Redlich−Kister Equation (Eq 4) and Standard Deviations (Eq 5)

T/K	a_0	a_1	a_2	σ
		V^E/cm^3·mol^{-1}		
288.15	−1.315	-5.127×10^{-2}	0.168	0.003
293.15	−1.497	-2.668×10^{-2}	0.190	0.002
298.15	−1.659	-6.325×10^{-2}	0.277	0.004
303.15	−1.787	-6.812×10^{-2}	0.297	0.005
308.15	−1.965	-13.971×10^{-2}	0.398	0.007
		$\delta\eta$/mPa·s		
288.15	0.418	0.022×10^{-3}	1.972×10^{-2}	0.001
293.15	0.317	1.497×10^{-2}	-5.301×10^{-2}	0.002
298.15	0.177	2.511×10^{-2}	0.017×10^{-2}	0.001
303.15	0.101	2.195×10^{-2}	-3.614×10^{-2}	0.001
308.15	0.059	1.002×10^{-2}	-4.701×10^{-2}	0.001

Results

Excess molar volumes V^E were calculated[5,6] from the measured densities (ρ) by using the relation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{1}$$

where ρ_{12} is the density of the mixture and M_1, x_1, ρ_1 and M_2, x_2, and ρ_2 are the molecular weight, mole fraction, and density of pure paraldehyde (1) and propylene carbonate (2), respectively. The experimental densities and calculated values of the excess molar volumes of binary mixtures of paraldehyde (1) + propylene carbonate (2) at five different temperatures are reported in Table 2.

Dynamic viscosities (η) of the binary mixture of paraldehyde (1) + propylene carbonate (2) mixtures at different temperatures were calculated from densities and flow times by using the relation

$$\eta = K\rho t \tag{2}$$

where K is the viscometer constant ($K = 0.01$, as given by the manufacturer) and ρ and t are the density and flow time of the mixture, respectively. The viscosity deviations of binary mixtures were calculated[7,8] by using the relation

$$\delta\eta = \eta - \Sigma x_i \eta_i \tag{3}$$

where η is the viscosity of the mixture, η_i is the viscosity of pure component i, and x_i is the mole fraction of component i. The calculated values of η and $\delta\eta$ are reported in Table 2.

The calculated excess molar volumes (V^E) and viscosity deviations ($\delta\eta$) were correlated by the Redlich−Kister polynomial[9] by using the relation

$$\Delta Y = x_1 x_2 \Sigma a_i (x_1 - x_2)^i \tag{4}$$

The coefficients in eq 4 were estimated by the least-squares fit method, and the standard deviation was calculated by using the relation

$$\sigma = \left[\frac{\Sigma(\Delta Y_{\text{exptl}} - \Delta Y_{\text{calcd}})^2}{D - N}\right]^{0.5} \tag{5}$$

where D and N are the number of data points and parameters, respectively.

Regression results for excess molar volumes and viscosity deviations of binary mixtures of paraldehyde (1) + propylene carbonate (2) at different temperatures are reported in Table 3.

Discussion

The sign and magnitude of V^E give a good estimate of the strength of the unlike interactions in the binary mixtures. Large positive values indicate weak interactions, whereas large negative values are observed when these interactions are strong and intermolecular complexes are believed to be present.[10]

In the present study, the values of V^E are found to be negative (Figure 1) over the entire range of compositions

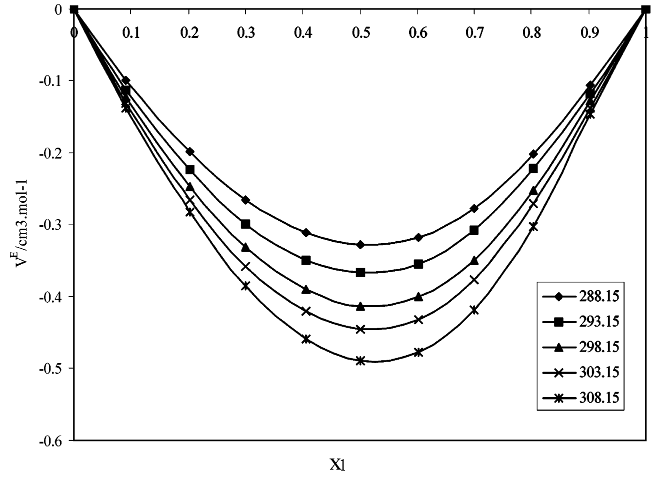

Figure 1. Excess molar volumes for binary mixtures of paraldehyde (1) + propylene carbonate (2) at (288.15, 293.15, 298.15, 303.15, and 308.15) K.

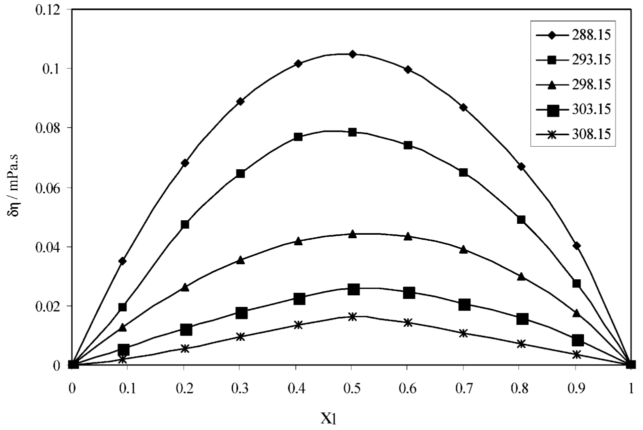

Figure 2. Viscosity deviations ($\delta\eta$) for binary mixtures of paraldehyde (1) + propylene carbonate (2) at (288.15, 293.15, 298.15, 303.15, and 308.15) K.

and for all the temperatures, indicating the presence of strong interactions between components of the mixtures. The maximum negative (or minima) value of excess molar volume occurs at x_1= 0.501 for all the temperatures studied. A considerable amount of volume contraction is observed from (288.15 to 308.15) K. The change in value of V^E in this temperature range is -0.161 cm^3·mol^{-1}.

The viscosity deviations ($\delta\eta$) are positive (Figure 2) over the entire range of compositions and for all temperatures studied, indicating the presence of strong interactions[11−13] between components of the mixtures. The maximum value of the viscosity deviation occurs at x_1 = 0.501 for all temperatures studied. The value of the viscosity deviation decreases as the temperature increases.[14]

Moreover, a specific interaction between unlike molecules is operating in the mixing process. This interaction can be responsible for the signs of V^E and $\delta\eta$. With an increase in temperature, the $\delta\eta$ value decreases because the increase in temperature makes these interactions far more difficult to take place. Consequently, the value of the viscosity deviation becomes less positive. At the same time, because of better interstitial accommodation due to thermal agitation, V^E becomes more negative.

Literature Cited

(1) Jahagirdar, D. V.; Arbad, B. R.; Walvekar, A. A.; Shankarwar, A. G.; Lande, M. K. Studies in Partial Molar Volumes, Partial Molar Compressibilities and Viscosity Coefficients of Caffeine in Water at Four Temperatures. *J. Mol. Liq.* **2000**, *85*, 361−373.

(2) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Techniques of Chemistry Series; Wiley: New York, 1986; Vol. 2, pp 74, 434, 990.

(3) Moumouzias, G.; Ritzoulis, G. Viscosities and Densities for Propylene Carbonate + Toluene at 15, 20, 25, 30 and 35 °C. *J. Chem. Eng. Data* **1992**, *37*, 482−483.

(4) Levitte, B. P. *Findlay's Practical Physical Chemistry*, 9th ed.; Longman Inc.: New York, 1973; p 430.

(5) Nikam, P. S.; Jagdale, B. S.; Sawant, A. B.; Hasan, M. Densities and Viscosities of Binary Mixtures of Toluene with Methanol, Ethanol, Propan-1-ol, Butan-1-ol, Pentan-1-ol, and 2-Methyl Propan-2-ol at (303.15, 308.15, 313.15) K. *J. Chem. Eng. Data* **2000**, *45*, 559−563.

(6) Nakanishi, K.; Hideko, S. Studies on Associated Solutions. I. Excess Volume of Binary Systems of Alcohols with Organic Liquids. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1634−1642.

(7) Dominguez, M.; Rodriguez, S.; Lopez, M. C.; Royo, F. M.; Urieta, J. S. Densities and Viscosities of Ternary Mixtures 1-Butanol + 1-Chlorobutane + 1-Butylamine and 2-Methyl-1-Propanol + 1-Chlorobutane + Butylamine at 298.15 K. *J. Chem. Eng. Data* **1996**, *41*, 37−42.

(8) Visak, Z. P.; Farreira, A. G. M.; Fonseca, I. M. A. Densities and Viscosities of Ternary Mixtures Water + Butyl Acetate + Methanol and Water + Ethyl Propionate + Methanol at 303.15 K. *J. Chem. Eng. Data* **2000**, *45*, 926−931.

(9) Redlich, O.; Kister, A. T. Thermodynamic of nonelectrolytic solutions. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.

(10) Suri, S. K.; Naorem, H. Thermodynamic Studies of Binary Mixtures of Tetrahydrofuran with Some Oxygen- and Nitrogen-Containing Solvents: Molar Excess Volumes. *J. Chem. Eng. Data* **1987**, *32*, 462−464.

(11) Agnihotri, S. C.; Prakash, O. Volumetric and Viscometric Studies of Binary Liquid Mixtures. *J. Chem. Eng. Data* **1989**, *34*, 5−7.

(12) Nath, J.; Tripathi, A. D. Viscosities of Binary Liquid Mixtures of 1,1,2,2-Tetrachloroethane with Benzene, Toluene, P-Xylene, Acetone and Cyclohexane. *Ind. J. Pure Appl. Phys.* **1986**, *24*, 541−545.

(13) Bilkis, A. B.; Biswas, S. K.; Alamgir, M.; Saleh, M. A. Viscosities and Excess Viscosities for Binary Liquid Mixtures of Ethylene Glycol with Water, Dioxan and Acetone at 30, 35, 40, 45 and 50 °C. *Ind. J. Chem.* **1996**, *35A*, 127−132.

(14) Weng, W. L. Densities and Viscosities for Binary Mixtures of Butylamine with Aliphatic Alcohols. *J. Chem. Eng. Data* **2000**, *45*, 606−609.

Received for review August 26, 2004. Accepted October 28, 2004.

JE0496903