Thermodynamic Properties of Water + Tetrahydrofuran and Water + 1,4-Dioxane Mixtures at (303.15, 313.15, and 323.15) K†

Jyoti N. Nayak, Mrityunjaya I. Aralaguppi, B. Vijaya Kumar Naidu, and Tejraj M. Aminabhavi*

Membranes Separations Division, Center of Excellence in Polymer Science, Karnatak University,
Dharwad 580 003, India

Properties like density and viscosity at (303.15, 313.15, and 323.15) K and refractive index at 303.15 K have been measured for binary mixtures of water + tetrahydrofuran and water + 1,4-dioxane. The excess molar volume (V^E) has been calculated from the density results. Viscosity and refractive index data have been used to compute respectively deviations in viscosity ($\Delta\eta$) and molar refraction (ΔR) of the mixtures. Excess molar volume and deviations in viscosity and molar refraction data have been fitted to the Redlich−Kister equation to calculate binary coefficients and standard deviations. Furthermore, literature published vapor−liquid equilibrium data of the mixtures have been used to construct $x-y$ composition curves and compared with the pervaporation curves. Results of this study indicate the importance of the pervaporation technique for the separation of mixtures over that of simple distillation at the azeotropic composition. Permeate samples were analyzed by refractive index as well as gas chromatography measurements to get the exact content of water.

Introduction

Tetrahydrofuran (THF) is a cyclic ether produced mainly from furfural. Due to its proton accepting nature, it is used as a solvent in many chemical industries. 1,4-Dioxane is a widely used solvent in paints, varnishes, lacquers, cosmetics, and deodorants as well as in pharmaceutical industries. Both these liquids are fully miscible with water in all proportions. Many chemical/pharmaceutical industries encounter problems in separating these liquids from aqueous waste streams, since these mixtures form azeotropes at lower compositions of water. Physicochemical properties of the mixtures of THF or 1,4-dioxane in water are important in process engineering[1] as well as in analyzing the membrane-based pervaporation (PV) separation data to separate water from its mixtures with 1,4-dioxane or THF.

Recently, we have used the PV technique[2,3] to separate the water−organic mixtures wherein we realized the importance of interactions between the components of the binary mixtures. Thus, we find it essential to calculate excess molar volume (V^E) and deviations in viscosity ($\Delta\eta$) and molar refraction (ΔR) from density (ρ), viscosity (η), and refractive index (n_D) data on mixtures that could be separated by the PV technique. In the present study, vapor−liquid equilibrium (VLE) data of the mixtures computed using the literature data[4,5] have been compared with the PV data to prove the superiority of the PV technique over that of simple distillation, particularly at the azeotropic composition (Table 7). Sodium alginate was used as a membrane in the PV experiments. Innumerable papers concerning thermodynamic data on aqueous−organic mixtures are already available in the earlier liteature,[6−12] but the present study is unique in that their relevance in membrane-based PV separation using a polymeric membrane is emphasized.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with Literature Values at 303.15 K

liquid	mol % purity	ρ/kg·m^{-3} expt	ρ/kg·m^{-3} lit.	n_D expt	n_D lit.
water	(>99.7)	995.71	995.7[6]	1.3326	1.3320[8]
tetrahydrofuran	(>99.7)	876.60	877.9[13]	1.4048	1.4028[13]
1,4-dioxane	(>99.0)	1024.63	1022.5[13]	1.4181	1.4180[13]

Experimental Section

Materials. High purity analytical reagent grade tetrahydrofuran was procured from s.d.fine-chem, Mumbai, India. HPLC grade 1,4-dioxane was purchased from Qualigens fine chemicals, Mumbai, India. The mole percent purities of these liquids as determined by GC (HP 6890) using a FID detector were >99. These data reported in Table 1 along with density and refractive index results measured at 303.15 K for pure liquids are compared with the literature values.[6,8,13] Sodium alginate, glutaraldehyde, acetone, and HCl were obtained from s.d.fine-chem, Mumbai, India. Double distilled deionized water was used throughout the study. The purity of the water was tested by its conductivity value, which agreed with the literature value (0.043×10^{-6} S·cm^{-1}) within 2%.

Measurements. Densities of pure liquids and their mixtures were measured with a high precision vibrating tube digital density meter, Anton Paar, DMA model 4500/5000 (Graz, Austria). The temperature in the measuring cell was automatically controlled within an uncertainty of ±0.01 K with an inbuilt integrated Pt 100 measuring sensor. The instrument was calibrated with air and double distilled and freshly degassed water at the temperature of measurement during every session. The densities of all the mixtures belonging to a given system (including pure components) were measured during one session. The experimental uncertainty (i.e., reproducibility of the measured densities) was up to five units in the second decimal place.

Before the samples were injected, adjustments were made if deviations between the displayed values and the

---

† CEPS Communication No. 1.

* To whom correspondence should be addressed. E-mail: aminabhavi@yahoo.com. Fax: 91-836-2771275.

10.1021/je030196t CCC: $27.50

reference values of the density standards exceeded the specifications of the instrument. Air and double distilled freshly degassed water were used for calibration. The density values of water and dry air at the specific atmospheric pressure are stored in the memory of the instrument for the complete temperature range investigated. If the compared values agreed within ±0.05 kg·m^{-3}, measurements were started after drying the measuring cell.

Viscosities were measured[14] using a Schott Gerate, model AVS 350 (Hofheim, Germany), Ubbelohde capillary viscometer. In this instrument, time measurement was fully automatic. The change in light intensity was converted to a digital electrical signal, and efflux times were determined on a digital display within an uncertainty of ±0.01 s. The viscometer was immersed in a thermostatic bath (Schott Gerate, model CT 050/2 (Hofheim, Germany)) and was electronically controlled to the set temperature. The uncertainty in temperature was ±0.01 K, while the uncertainty in viscosity was ±0.001 mPa·s. Approximately, a 5 cm^3 volume of the liquid was placed in the viscometer, the liquid was allowed to equilibrate to the desired bath temperature for about 10 min, and the viscosity of the liquid or liquid mixture was calculated using the relation

$$\eta = tk\rho \tag{1}$$

where k is the viscometer constant (0.1111 mm^2·s^{-2}), ρ is the density of the liquid, and t is the efflux time in seconds.

Refractive indices (n_D) for the sodium D-line were measured using a thermostatically controlled Abbe Refractometer, Atago, model 3T (Tokyo, Japan). The uncertainty in the refractive index is ±0.0001. At least three independent readings of all the physical properties (ρ, η, and n_D) were taken for each mole fraction of the mixture, and averages of these values are reported in Table 2.

A sodium alginate (NaAlg) membrane was prepared by dissolving 5 g of NaAlg in 100 mL of distilled water in a 250 mL beaker. The solution was filtered through a cotton plug, poured on a glass plate, and evaporated to dryness in a dust free atmosphere at room temperature. The membrane formed was peeled off from the glass plate and cross-linked by immersion in an acidic methanol solution and water in the ratio 75:25 containing 1 vol % glutaraldehyde for 12 h. The membrane was dried at room temperature. The membrane thickness as measured by a micrometer screw gauge was 30 ± 2 μm.

Pervaporation experiments were performed in an apparatus designed indigenously[15] (see Figure 1). The PV apparatus consists of a stirred stainless steel cell through which retentate is circulated to the feed tank. The effective surface area of the membrane in the cell is 32.43 cm^2 with a diameter of 6.4 cm, and the volume capacity of the cell is 250 cm^3. The temperature of the feed mixture is kept constant using a thermostatic water jacket. The PV cell is provided with an efficient three-blade stirrer powered by a dc current motor in the feed compartment. Turbulent flows were obtained even at a low rotation of the stirrer, that is, below 200-rpm speed. The mass transfer limitation due to concentration polarization is negligible. The downstream side of the PV apparatus was continuously evacuated using a vacuum pump (Toshniwal, Mumbai, India) at a low pressure, 1.33 kPa.

The test membrane was equilibrated for about 3 h with the feed mixture before starting the PV experiment. After establishment of a steady state, permeate vapors were collected in traps immersed in liquid nitrogen. PV experiments were performed with a sodium alginate membrane for the binary mixtures containing 5−50 mass % water.

Table 2. Experimental Density (ρ), Viscosity (η), and Refractive Index (n_D) of Binary Mixtures at Different Temperatures

x_1	ρ/kg·m^{-3}	η/mPa·s	n_D
Water (1) + Tetrahydrofuran (2)			
303.15 K			
0.0	876.60	0.463	1.4048
0.3081	894.98	0.574	1.3994
0.5004	912.11	0.793	1.3946
0.6319	927.10	1.001	1.3870
0.7276	941.82	1.208	1.3786
0.8002	955.23	1.344	1.3684
0.8573	966.73	1.384	1.3613
0.9034	977.20	1.341	1.3546
0.9413	984.94	1.226	1.3405
0.9730	990.31	1.003	1.3386
1.0	995.71	0.754	1.3326
313.15 K			
0.0	865.65	0.400	
0.3081	884.04	0.519	
0.5004	901.53	0.668	
0.6319	916.82	0.833	
0.7276	931.96	0.980	
0.8002	945.99	1.061	
0.8573	958.34	1.084	
0.9034	969.74	1.021	
0.9413	984.94	0.920	
0.9730	990.31	0.803	
1.0	991.91	0.624	
323.15 K			
0.0	854.30	0.372	
0.3081	872.90	0.340	
0.5004	890.70	0.578	
0.6319	901.63	0.698	
0.7276	921.90	0.807	
0.8002	936.50	0.868	
0.8573	949.30	0.871	
0.9034	962.20	0.829	
0.9413	972.70	0.740	
0.9730	980.80	0.641	
1.0	985.70	0.544	
Water (1) + 1,4-Dioxane (2)			
303.15 K			
0.0	1024.63	1.022	1.4181
0.3523	1029.10	1.205	1.4116
0.5503	1032.40	1.413	1.4046
0.6772	1033.83	1.563	1.3972
0.7654	1033.22	1.573	1.3910
0.8304	1030.50	1.497	1.3865
0.8801	1025.60	1.362	1.3798
0.9195	1019.51	1.194	1.3698
0.9514	1012.10	1.070	1.3517
0.9778	1004.10	0.876	1.3417
1.0	995.71	0.754	1.3326
313.15 K			
0.0	1013.3	0.871	
0.3523	1018.5	1.005	
0.5503	1022.6	1.157	
0.6772	1024.7	1.257	
0.7654	1024.7	1.279	
0.8304	1022.7	1.216	
0.8801	1018.7	1.120	
0.9195	1013.4	0.986	
0.9514	1006.9	0.869	
0.9778	999.80	0.735	
1.0	992.30	0.624	
323.15 K			
0.0	1001.9	0.807	
0.3523	1007.8	0.866	
0.5503	1012.5	0.982	
0.6772	1015.2	1.029	
0.7654	1015.9	1.034	
0.8304	1014.6	0.998	
0.8801	1011.4	0.884	
0.9195	1006.9	0.809	
0.9514	1001.3	0.728	
0.9778	994.90	0.613	
1.0	988.10	0.544	

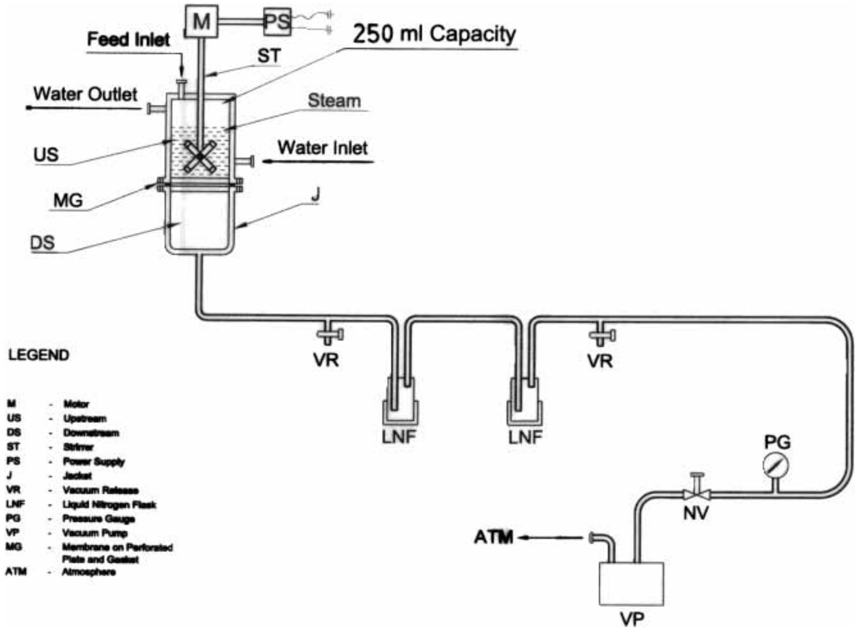

Figure 1. Schematic diagram of the indigenously designed PV laboratory set up.

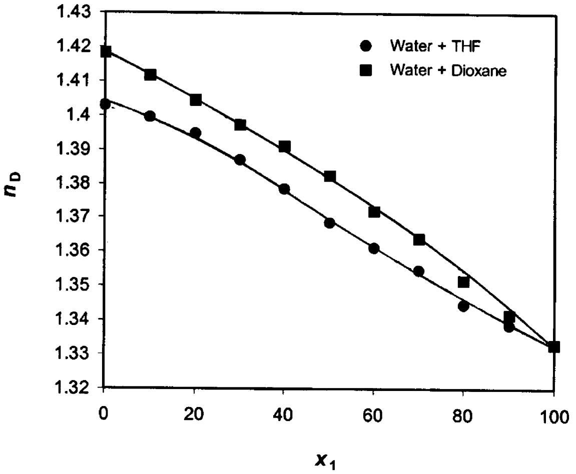

Figure 2. Refractive index data for water (1) + THF (2) (●) and water (1) + 1,4-dioxane (2) (■) mixtures at 303.15 K.

These mixture composition ranges were particularly chosen because the PV technique is effective at lower compositions of water. Such mixtures are difficult to separate by the conventional distillation technique, since they are known to form azeotropes at lower compositions of water.

During the progress of the PV experiment, a required quantity of the solvent mixture was added continuously to enrich the amount of liquid permeated through the membrane from the feed compartment. The mass of permeate collected in the trap was measured on a digital Mettler balance, model AE 240 (Greifensee, Switzerland), and its composition was determined at 303.15 K by measuring its refractive index and by comparing it with the standard plot of refractive index at 303.15 K versus mole fraction of both the mixtures (see Figure 2). A minimum of three readings was taken, but average values were considered in all the calculations. The mixture composition for PV experiments was based on mass percent, but while the PV curves were being plotted, mass percent was converted to mole fraction.

For water + THF mixtures, feed and permeate samples at a low water composition (0.05 mole fraction) were analyzed using a Nucon gas chromatograph, model 5765 (Mumbai, India), installed with a thermal conductivity detector (TCD) and a packed DEGS column of $^1/_8$ in. i.d. and 2 m length. The oven temperature was maintained at 70 °C (isothermal) while the injector and detector temperatures were maintained at 150 °C. The sample injection size was 1 μL, and pure hydrogen was used as a carrier gas at a pressure of 1 kg/cm^2. The GC response was calibrated for this particular column and conditions with known compositions of water + THF mixtures; calibration factors were fed into the software to obtain the correct analysis for unknown samples. The same procedure was adapted for the analysis of water + 1,4-dioxane mixtures using a packed Tenax column of $^1/_8$ in. i.d. and 2 m length. The GC conditions remained the same, and the GC response was calibrated for the Tenax column.

Results and Discussion

Excess molar volume (V^E) values of the aqueous−organic mixtures were calculated using the equation

$$V^E = V_m - V_1x_1 - V_2x_2 \qquad (2)$$

where V_m is the molar volume of the mixture and V_1 and V_2 are the molar volumes of pure components 1 and 2 of the mixture. These data at (303.15, 313.15, and 323.15) K are presented in Table 3 and displayed in Figure 3. For both the mixtures, V^E data are negative. In the case of a water + THF mixture at $x_1 = 0.63$, V^E is -0.80×10^{-6} m^3·mol^{-1}, whereas, for a water + 1,4-dioxane mixture, $V^E = -0.69 \times 10^{-6}$ m^3·mol^{-1} at $x_1 = 0.67$. A large negative V^E observed for a water + THF mixture is attributed to higher specific interactions between water and THF molecules due to large differences in their dielectric constant and dipole moment values when compared to the difference between water and 1,4-dioxane molecules. In the present mixtures, we have not observed any wide variations in V^E values within the investigated range of temperature (see Figure 3). Smoothed curves were drawn from the best-fitted values, giving minimum standard errors. A comparison of the present V^E values at 303.15 K with the literature data[7] at 298.15 K for equimolar composition showed agreement within 6.3% for water + 1,4-dioxane mixtures and within 2.8% for water + THF mixtures. Such small differences may be due to differences in the experimental temperature between the present data and the literature data.[7]

Table 3. Excess Molar Volume (V^E) Data of the Binary Mixtures at Different Temperatures

	10^6V^E/m^3·mol^{-1}				10^6V^E/m^3·mol^{-1}		
x_1	303.15 K	313.15 K	323.15K	x_1	303.15 K	313.15 K	323.15K
	Water (1) + THF (2)				Water (1) + 1,4-Dioxane (2)		
0.3081	−0.5425	−0.5237	−0.5169	0.3523	−0.4468	−0.4492	−0.4547
0.5004	−0.7702	−0.7509	−0.7503	0.5503	−0.6423	−0.6481	−0.6554
0.6319	−0.8033	−0.7756	−0.7726	0.6772	−0.6984	−0.6983	−0.7020
0.7276	−0.7997	−0.7679	−0.7667	0.7654	−0.6700	−0.6658	−0.6666
0.8002	−0.7400	−0.7102	−0.7112	0.8304	−0.5885	−0.5831	−0.5817
0.8573	−0.6301	−0.6059	−0.6053	0.8801	−0.4735	−0.4680	−0.4668
0.9034	−0.5088	−0.4903	−0.5111	0.9195	−0.3533	−0.3487	−0.3475
0.9413	−0.3459	−0.3432	−0.3728	0.9514	−0.2266	−0.2244	−0.2247
0.9730	−0.1595	−0.1670	−0.2051	0.9778	−0.1087	−0.1075	−0.1078

Table 4. Results of Viscosity Deviations ($\Delta\eta$) of the Binary Mixtures at Different Temperatures

	$\Delta\eta$/mPa·s				$\Delta\eta$/mPa·s		
x_1	303.15 K	313.15 K	323.15K	x_1	303.15 K	313.15 K	323.15 K
	Water (1) + THF (2)				Water (1) + 1,4-Dioxane (2)		
0.3081	0.022	0.050	−0.085	0.3523	0.274	0.221	0.152
0.5004	0.184	0.156	0.121	0.5503	0.538	0.420	0.319
0.6319	0.362	0.291	0.217	0.6772	0.722	0.552	0.400
0.7276	0.533	0.416	0.309	0.7654	0.756	0.597	0.428
0.8002	0.648	0.482	0.359	0.8304	0.697	0.549	0.409
0.8573	0.672	0.492	0.352	0.8801	0.576	0.465	0.308
0.9034	0.615	0.418	0.302	0.9195	0.418	0.341	0.244
0.9413	0.489	0.309	0.206	0.9514	0.303	0.232	0.171
0.9730	0.257	0.185	0.102	0.9778	0.116	0.104	0.063

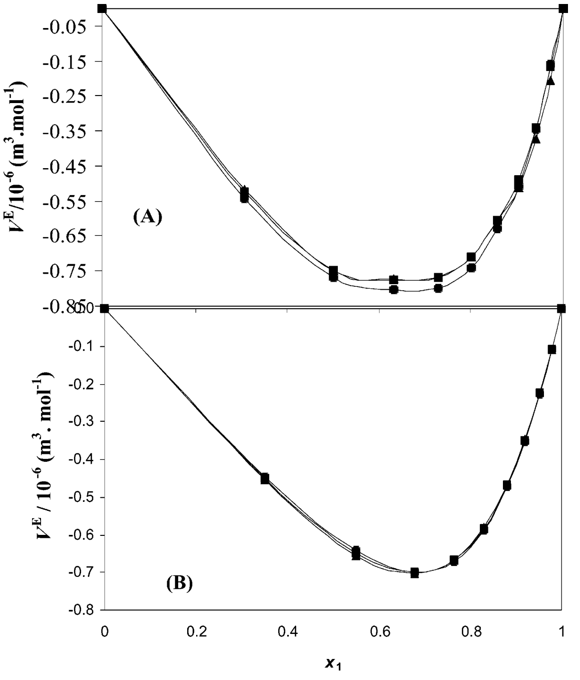

Figure 3. Plots of V^E vs mole fraction of water in (A) water (1) + THF (2) and (B) water (1) + 1,4-dioxane (2) mixtures at (●) 303.15, (■) 313.15, (▲) and 323.15 K.

Table 5. Results of Deviations in Molar Refraction (ΔR) of Viscous Flow for the Binary Mixtures at 303.15 K

x_1	$10^6\Delta R$/m^3·mol^{-1}	x_1	$10^6\Delta R$/m^3·mol^{-1}
Water (1) + THF (2)		Water (1) + 1,4-Dioxane (2)	
0.3081	0.003	0.3523	0.002
0.5004	0.004	0.5503	0.004
0.6319	0.003	0.6772	0.005
0.7276	0.002	0.7654	0.008
0.8002	−0.002	0.8304	0.012
0.8573	−0.002	0.8801	0.014
0.9034	−0.001	0.9195	0.012
0.9413	−0.008	0.9514	0.002
0.9730	−0.002	0.9778	0.001

Using the results of viscosity and refractive index, deviations in viscosity ($\Delta\eta$) and molar refractivity (ΔR) have been calculated from a general equation of the type[16,17]

$$\Delta Y = Y_m - Y_1x_1 - Y_2x_2 \tag{3}$$

where ΔY represents deviations in $\Delta\eta$ or ΔR, respectively, Y_1 and Y_2 are the respective pure liquid viscosities or molar refractivities of the pure components 1 and 2 of the mixture, and Y_m refers to the respective properties of the mixtures. Molar refractivity (R) was calculated using the Lorenz−Lorentz relation. For calculating ΔR values of the mixtures, volume fraction ($\phi_i = x_iv_i/\sum_{i=1}^{2} x_iv_i$) was used.[13,16,17]

Calculated values of $\Delta\eta$ are presented in Table 4 while those of ΔR at 303.15 K are presented in Table 5. Results of $\Delta\eta$ versus x_1 at (303.15, 313.15, and 323.15) K are displayed in Figure 4. For both the mixtures, curves show somewhat sigmoidal trends. Particularly, in the case of water + 1,4-dioxane mixtures, $\Delta\eta$ values at lower compositions of water are higher than those observed for water + THF mixtures. As the composition of water in the binary mixture increases, mixture polarity increases, thereby showing an increase in $\Delta\eta$ values. Maximum $\Delta\eta$ values are observed between 0.70 and 0.75 mPa·s for both the mixtures at around $x_1 = 0.8$. This indicates that the flow behavior of the mixtures is almost identical at higher compositions of water. Figure 5 displays the dependence of ΔR on ϕ_1. Here, the shapes of the curves are widely different for both the mixtures.

The calculated quantities (V^E, $\Delta\eta$, and ΔR) have been fitted to the Redlich and Kister[18] equation by the method of least-squares using the Marquardt algorithm[19] to derive the binary coefficients (A_j) and to estimate the standard deviation (σ) as follows:

$$(\Delta Y) = x_1x_2\sum_{j=1}^{k}A_j(x_2 - x_1)^{j-1} \tag{4}$$

In each case, the optimum number of coefficients A_j was

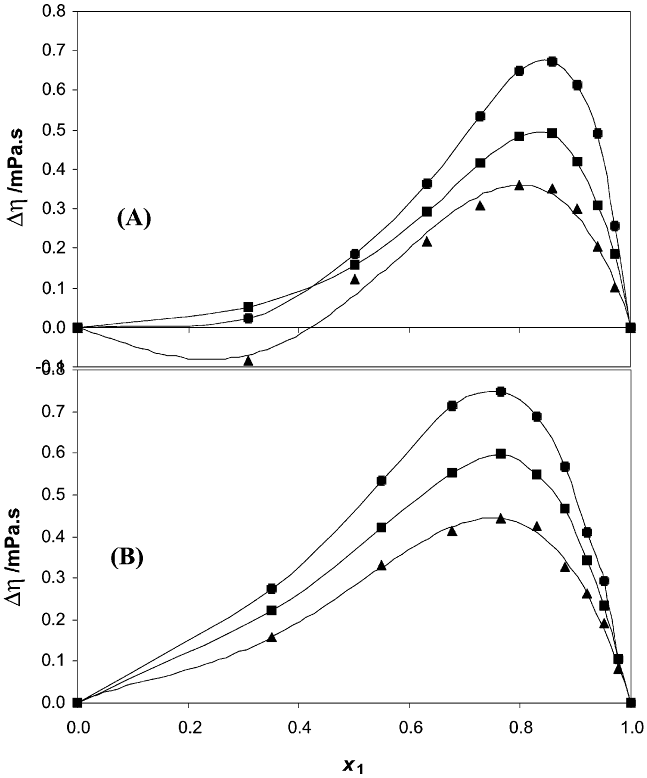

Figure 4. Plots of $\Delta\eta$ vs mole fraction of water in (A) water (1) + THF (2) and (B) water (1) + 1,4-dioxane (2) mixtures at (●) 303.15, (■) 313.15, (▲) and 323.15 K.

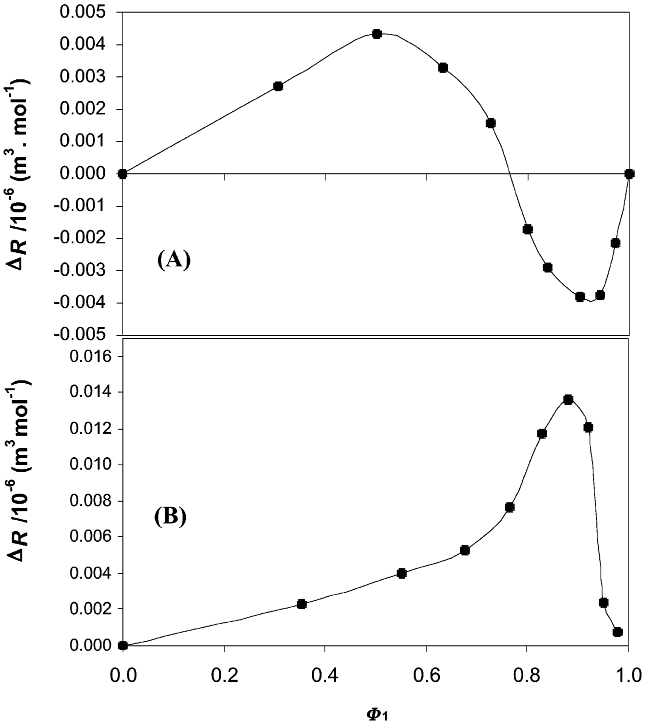

Figure 5. Plots of ΔR vs volume fraction of water in (A) water (1) + THF (2) and (B) water (1) + 1,4-dioxane (2) mixtures at (●) 303.15 K.

Table 6. Derived Parameters of Eq 4 for Various Functions of Binary Mixtures at Different Temperatures

function	T/K	A_1	A_2	A_3	σ
	Water (1) + THF (2)				
10^6V^E/m^3·mol^{-1}	303.15	−2.939	1.662	−1.982	0.033
	313.15	−2.731	1.528	−2.754	0.127
	323.15	−2.465	1.031	−3.642	0.130
$\Delta\eta$/mPa·s	303.15	0.427	−2.779	6.084	0.052
	313.15	0.279	−2.993	6.076	0.066
	323.15	0.310	−2.284	1.640	0.025
$10^6\Delta R$/m^3·mol^{-1}	303.15	−21.36	15.37	−10.99	0.239
	313.15	−25.13	19.63	−15.05	0.330
	323.15	−25.41	19.93	−15.09	0.343
	Water (1) + 1,4-Dioxane (2)				
10^6V^E/m^3·mol^{-1}	303.15	−2.407	1.852	−1.172	0.006
	313.15	−2.433	1.847	−1.034	0.005
	323.15	−2.450	1.801	−1.060	0.004
$\Delta\eta$/mPa·s	303.15	1.919	−3.092	2.069	0.019
	313.15	1.477	−2.338	1.932	0.011
	323.15	1.102	−1.806	1.045	0.042
$10^6\Delta R$/m^3·mol^{-1}	303.15	−23.02	18.34	−13.70	0.242
	313.15	−26.83	21.42	−15.63	0.349
	323.15	−27.09	21.74	−15.90	0.348

Table 7. Pervaporation and Vapor−Liquid Equilibrium Data for the Binary Mixtures of Water (1) + THF (2) and Water (1) + 1,4-Dioxane (2) at 303.15 K

pervaporation (present data)		vapor−liquid equilibrium[4]		pervaporation		vapor−liquid equilibrium[5]	
x_1	y_1	x_1	y_1	x_1	y_1	x_1	y_1
Water (1) + THF (2)				Water (1) + 1,4-Dioxane (2)			
0.200	0.942	0.972	0.300	0.200	0.910	0.996	0.958
0.352	0.890	0.962	0.255	0.308	0.710	0.989	0.914
0.550	0.796	0.955	0.233	0.500	0.537	0.979	0.863
0.677	0.755	0.925	0.219	0.632	0.495	0.958	0.774
0.765	0.668	0.884	0.203	0.728	0.490	0.941	0.711
0.830	0.663	0.817	0.200	0.800	0.482	0.914	0.628
		0.772	0.198			0.888	0.567
		0.736	0.200			0.863	0.533
		0.646	0.198			0.851	0.521
		0.559	0.197			0.801	0.489
		0.469	0.195			0.757	0.464
		0.389	0.190			0.728	0.451
		0.302	0.180			0.669	0.428
		0.235	0.168			0.550	0.403
		0.202	0.160			0.451	0.387
		0.132	0.135			0.369	0.369
		0.112	0.130			0.284	0.350
		0.078	0.099			0.223	0.332
		0.044	0.064			0.184	0.314
		0.024	0.035			0.134	0.295
						0.090	0.255
						0.066	0.217
						0.036	0.153
						0.013	0.081

determined from an examination of the variation of standard deviation *(σ)* calculated by using

$$\sigma = [\sum(\Delta Y_{\mathrm{cal}} - \Delta Y_{\mathrm{obs}})^2/(n - m)]^{1/2} \qquad (5)$$

Here, *n* is the number of measurements and *m* is the number of coefficients used in fitting the data. Estimated values of A_j and σ for V^E, $\Delta\eta$, and ΔR are presented in Table 6. In all the cases, the best fit was obtained by using only three adjustable fitting coefficients in eq 4. The curves shown in Figures 3−5 were drawn using the smoothed values calculated from eqs 4 and 5, which produced the lowest errors.

VLE data on binary mixtures are extremely important in understanding the binary interactions between liquid components. Using the vapor pressure data of liquids and liquid mixtures, one can compute the mole fractions of the components in the vapor and the liquid phases. In process engineering applications, such data have relevance, particularly if one is concerned about the separation of azeotropic mixtures. From the PV separation experiments, we have computed the mole fraction data in both vapor and liquid phases from refractometry as well as gas chroma-

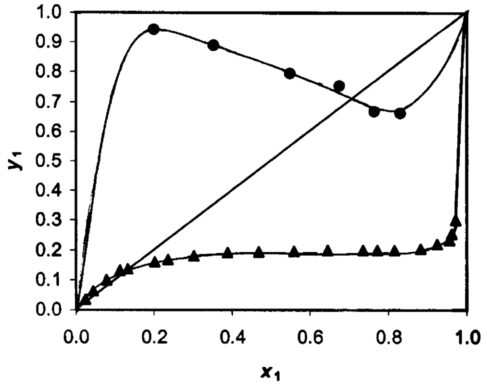

Figure 6. Comparison of the vapor−liquid equilibrium curve (▲) with PV data (●) for the water (1) + THF (2) mixture at 303.15 K.[4]

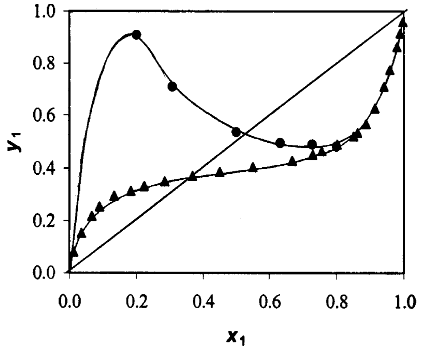

Figure 7. Comparison of the vapor−liquid equilibrium curve (▲) with PV data (●) for the water (1) + 1,4-dioxane (2) mixture at 303.15 K.[5]

tography experiments (at lower water compositions). The VLE data of these systems were not reported in the literature at 303.15 K; therefore, the literature data chosen for the comparison were those at temperatures close to 303.15 K, as far as possible. Comparisons with the literature VLE data for water + THF systems[4] at 323.15 K and water + 1,4-dioxane systems[5] at 308.15 K are presented in Figures 6 and 7. The azeotropic points for these systems at 303.15 K, estimated on the basis of all other literature VLE data, were $x_1 = 0.10$ and $x_1 = 0.37$ for water + THF and water + 1,4-dioxane, respectively. However, the azeotropic points are weakly dependent on temperature. Thus, separation of water from these mixtures by simple distillation is not feasible due to the low relative volatility of the mixture.

The PV curve shown in Figure 6 for water + THF and that of water + 1,4-dioxane shown in Figure 7 are well above the azeotropic compositions, as displayed by the VLE curves, indicating that the membrane acts as a third phase, which selectively allows water molecules to pass through due to a preferential affinity of water molecules for the barrier membrane. Thus, the PV technique has overcome the azeotropic barrier. At higher compositions of water in the liquid phase, the PV curve cuts a diagonal line at 0.55 mole fraction of water in the liquid phase for water + 1,4-dioxane mixtures while that for water + THF mixtures cuts a diagonal line at 0.68, indicating a pseudoazeotropic nature of the mixture at these compositions. In azeotropic distillation, however, a small amount of entrainer (generally, an environmentally hazardous organic compound) is usually added as a third phase to break the azeotrope, thus making the process less ecofriendly. In the present research, the membrane acts as a third phase, and thus, the process becomes environmentally clean.

Conclusions

This paper reports experimental data on density and viscosity at three temperatures, (303.15, 313.15, and 323.15) K, and on refractive index at 303.15 K. Excess molar volumes as well as deviations in viscosity and molar refractivity calculated from these data have been discussed in relation to their interactions as well as in PV separation problems. Pervaporation separation data are compared with VLE results obtained from the literature[4,5] for both the mixtures to demonstrate the superiority of the PV technique over that of simple distillation, particularly while separating aqueous−organic (1,4-dioxane or THF) azeotropes using a sodium alginate barrier membrane at the azeotropic compositions of the mixtures.

Acknowledgment

We thank Ms. Lakshmi Shetty for getting PV data in her M.E. project.

Literature Cited

(1) Seader, J. D.; Henley, E. J. *Separation Process Principles*; John Wiley & Sons: New York, 1998.

(2) Kurkuri, M. D.; Kumbar, S. G.; Aminabhavi, T. M. Syntheses and Characterization of Polyacrylamide Grafted Sodium Alginate Copolymeric Membranes and Their use in Pervaporation Separation of Water + Tetrahydrofuran Mixtures. *J. Appl. Polym. Sci.* **2002**, *86*, 272−281.

(3) Kurkuri, M. D.; Aminabhavi, T. M. Pervaporation Separation of Water and Dioxane Mixtures with Polyacrylamide-*g*-Sodium Alginate Copolymeric Membranes. *J. Appl. Polym. Sci.* **2003**, *89*, 300−305.

(4) Matous, J.; Novak, J. P.; Sobr, J.; Pick, J. Phase Equlibria in the System Tetrahydrofuran (1) − Water (2). *Collect. Czech. Chem. Commun.* **1972**, *37*, 2653−2663.

(5) Steinbrecher, M.; Bittrich, H. J. New Boiling Point and Dew Point Apparatus for the Determination of *px* (Pressure-Composition)-Diagrams of Multicomponent Systems. *Z. Phys. Chem. (Leipzig)* **1963**, *224*, 97−109.

(6) Lee, M.-J.; Hwang, S.-M.; Kuo, Y.-C. Densities and Viscosity of Binary Solutions Containing Butylamine, Benzylamine and Water. *J. Chem. Eng. Data* **1993**, *38*, 577−579.

(7) Aminabhavi, T. M.; Bindu, G. Density, Viscosity, Refractive Index and Speed of Sound in Aqueous Mixtures of *N*,*N*-Dimethylformamide, Dimethyl Sulfoxide, *N*,*N*-Dimethylacetamide, Acetonitrile, Ethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40*, 856−861.

(8) Tsierkezos, N. G.; Molinou, I. E. Thermodynamic Properties of Water + Ethylene Glycol at 283.15, 293.15, 303.15, and 313.15 K. *J. Chem. Eng. Data* **1998**, *43*, 989−993.

(9) Pal, A.; Singh, Y. P. Excess Molar Volumes and Apparent Molar Volumes of Some Amide + Water Systems at 303.15 and 308.15 K. *J. Chem. Eng. Data* **1995**, *40*, 818−822.

(10) Chen, G.; Knapp, H. Densities and Excess Molar Volumes for Sulfolane + Ethylbenzene, Sulfolane + 1-Methylnaphthalene, Water + *N*,*N*-Dimethylformamide, Water + Methanol, Water + *N*-Formylmorpholine, and Water + *N*-Methylpyrrolidone. *J. Chem. Eng. Data* **1995**, *40*, 1001−1004.

(11) Zielkiewicz, J. Excess Molar Volumes and Excess Gibbs Energies in *N*-Methylformamide + Water, or + Methanol, or + Ethanol at the Temperature (303.15) K. *J. Chem. Eng. Data* **1998**, *43*, 650−652.

(12) Marzal, P.; Monton, J. B.; Rodrigo, M. A. Isobaric Vapor-Liquid Equilibria of the Water + 2-Propanol System at (30, 60, and 100) kPa. *J. Chem. Eng. Data* **1996**, *41*, 608−611.

(13) Aminabhavi, T. M.; Patil, V. B. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Ethylbenzene with *N*,*N*-Dimethylacetamide, Tetrahydrofuran, *N*,*N*-Dimethylformamide, 1,4-Dioxane, Dimethyl Sulfoxide, Bromoform and 1-Chloronaphthalene in the Temperature Interval (298.15−308.15) K. *J. Chem. Eng. Data* **1998**, *43*, 497−503.

(14) Aminabhavi, T. M.; Banerjee, K. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of 2-Chloroethanol with Alkanols (C_1−C_6) at 298.15, 303.15, and 308.15. K *J. Chem. Eng. Data* **1998**, *43*, 509−513.

(15) Aminabhavi, T. M.; Naik, H. G. Pervaporative Dehydration of Water/Dimethyl Formamide Mixture Through Poly(Vinyl alcohol)-*g*-Polyacrylamide Coploymeric Membranes. *J. Appl. Polym. Sci.* **2002**, *83*, 273−282.
(16) Nayak, J. N.; Aralaguppi, M. I.; Aminabhavi, T. M. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Ethyl Chloroacetate with Hexane, Heptane, Octane, Nonane, Decane, and Dodecane. *J. Chem. Eng. Data* **2001**, *46*, 891−896.
(17) Aralaguppi, M. I.; Aminabhavi, T. M.; Balundgi, R. H. Excess Molar volume, Excess Isentropic Compressibility and Excess Molar Refraction of Binary Mixtures of Methyl Acetoacetate with Benzene, Toluene, *m*-Xylene, Mesitylene, and Anisole. *Fluid Phase Equilib.* **1992**, *71*, 99−112.
(18) Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345−348.
(19) Marquardt, D. W. An Algorithm for Least Squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431−441.

Received for review June 30, 2003. Accepted January 20, 2004. The authors thank the University Grants Commission (UGC), New Delhi, India, for major financial support (F1-41/2001/CPP-II) to establish the Center of Excellence in Polymer Science. M.I.A. and J.N.N. thank the Department of Science and Technology, New Delhi, India (SP/S1/H-09/2000), for financial support. B.V.K.N. thanks the Council of Scientific and Industrial Research, New Delhi, India (Grant No. 80(0042)/02/EMR-II), for awarding a research associateship.

JE030196T