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Isothermal Vapor−Liquid Equilibrium for Binary Mixtures of Polyoxyethylene 4-Octylphenyl Ether with Methanol, Ethanol, or Propan-2-ol

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ABSTRACT: A static-type phase equilibrium apparatus was installed to measure isothermal vapor−liquid equilibrium (VLE) data of polyoxyethylene 4-octylphenyl ether (POEOPE), commonly known as polyethylene glycol mono-4-octylphenyl ether, with methanol at (341.0 to 403.1) K, POEOPE + ethanol at (342.6 to 454.1) K, and POEOPE + propan-2-ol at (350.1 to 453.3) K. With a given feed composition, equilibrium pressures were measured at constant temperatures to obtain $p-T-x$ data. The experimental data were correlated with the Antoine equation. Those VLE data were also correlated with the universal quasichemical (UNIQUAC) and the nonrandom two-liquid (NRTL) activity coefficient models, respectively. The correlation results showed good agreement between the calculated values and the experimental data. The solvent activities calculated from the NRTL model are generally consistent with the values evaluated from the smoothed experimental results.

INTRODUCTION

The use of oligomers, such as the poly(ethylene glycol) class or PEGs, has been increasing in industry for the past few years.[1] PEG class belongs to a family of polymers that exhibit very different thermodynamic properties according to the molecular weight. The low molecular weight members of this series are commercially available in a range of viscous fluids to wax-like solids, while the higher molecular weight ones are thermoplastic-capable. PEG functional structures are attractive in industrial uses since the repeating unit of PEGs is like an open crown ring ether, which gives peculiar interactions with some molecules or ions.[2] Especially, PEGs have specific interactions between the ether oxygen and water due to hydrogen-bond formation.[3] These polymers can be found in linear or branched forms and are non-toxic and soluble in water as well as in many organic solvents (e.g., methylene chloride, ethanol, toluene, acetone, and chloroform). These properties, combined with the availability of PEGs with a wide range of end functions, contribute to the wide variety of applications in the pharmaceutical, chemical, cosmetic, and food industries and purification of biological materials.[4,5]

Polyoxyethylene 4-octylphenyl ether (POEOPE), a member of glycol ethers, specifically finds a broad range of applications due to its unique chemical composition and is extensively used in biological systems,[6−8] defoamers, emulsifiers, pesticide formulations,[9] industrial detergent formulations and wetting agents,[10] and wetting agents as an industrial cleaner.[11] As a consequence, the knowledge of vapor−liquid equilibrium (VLE) behavior of the relevant oligomeric mixtures is extremely important for development of the processing technology.

The saturated vapor pressure measurement is one of the most important properties since more than 80 % of literature VLE data of binary polymer solutions were obtained from this way. The vapor pressure data can be used directly in the determination of model parameters and then the models can be applied to calculate other useful thermodynamic properties. Although vapor pressure data for some polymer solutions have been compiled in open literature;[12−15] however, the database for polymer solutions is still modest in comparison with the enormous amount of data for conventional organic mixtures, and the specialized experimental database for oligomeric systems is especially scarce.[1] In the present study, the vapor pressure data are measured for the binary systems of POEOPE with methanol, ethanol, or propan-2-ol at temperatures ranging from (340 to 455) K. Although there are some VLE data for the mixtures of PEG/alcohols[16−20] and other ethylene glycol oligomers/alcohols in literature,[1,21−27] there are no VLE data available for the systems of POEOPE/alcohols at the comparable conditions of this work. The relationship between the saturated vapor pressure and temperature was correlated with the Antoine equation, and the constants were determined by nonlinear regression as well. Activity coefficient models, the universal quasichemical (UNIQUAC) equation,[28] and the nonrandom two-liquid (NRTL) equation[29] were applied to correlate the experimental data. These two thermodynamic models were further used to calculate solvent activities at various temperatures to observe the deviation from ideal behavior and compare with the values obtained from experimental results.

EXPERIMENTAL SECTION

Materials. Organic solvents, including methanol, ethanol, and propan-2-ol, were supplied by Aldrich Chemical Co. (USA) with the purity levels better than 0.998 in mass fraction and were used without further purification. The fractionation cut

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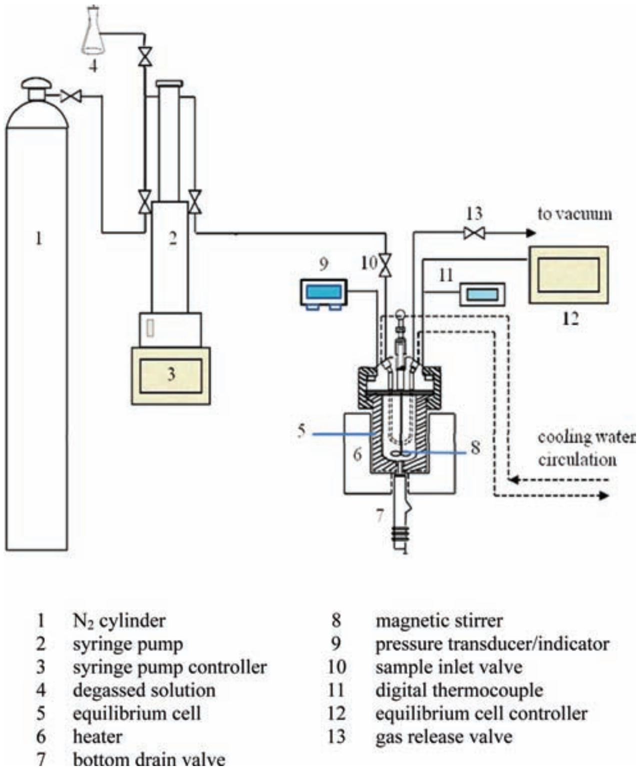

Figure 1. Schematic diagram of VLE measurement apparatus.

of polyethylene glycol mono-4-octylphenyl ether, known as polyoxyethylene 4-octylphenyl ether (POEOPE, CAS: 9002-93-1, $C_8H_{17}C_6H_4(OCH_2CH_2)_nOH$, n ca. 10), was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). Its average molecular weight (M_n) is about 647 $g \cdot mol^{-1}$.

Apparatus. A schematic diagram of the experimental apparatus is shown in Figure 1. It was modified from high pressure/high temperature (HP/HT) 4576 reactor (Parr Instrument Company, USA). The advantages of this apparatus and method are the simplicity and ease of operation for viscous samples like oligomeric solutions, wide ranges of operating temperature and pressure, and so forth. The equilibrium cell (**5**) has nominal size of 250 cm^3 and maximum working capacity of 187 cm^3 and is made of 316 stainless steel with the maximum pressure rating up to 34.5 MPa at 773 K. A heater (**6**) surrounds the equilibrium cell for heating purposes. The cell is also equipped with a controller series 4843 (**12**) that consists of a packaged temperature control unit completely wired and assembled with appropriate power and safety relays, switches, and pilot lights. This unit is designed specifically for use with the Parr reactor and equipped with: (a) variable stirrer speed control/optical tachometer to control the magnetic stirrer (**8**) and to achieve uniform mixing, ranging from (0 to 1999) rpm with ± 10 rpm accuracy; (b) digital pressure transducer which continuously monitoring the pressure within the equilibrium cell with 1 psi resolution; (c) digital high-temperature cutoff along with electrical heater switch, which provides a redundant high temperature safety cutoff which will shut down the cell if an unusual malfunction should develop in the primary control system. This module has its own thermocouple (**11**, J-type), digital display, and wiring and can be preset to shut down the cell at any desired temperature and (d) a digital ammeter display module which provides a means for continuously monitoring the current being drawn by the stirrer motor.

The HP/HT 4576 reactor has two valves mounted on the bomb head: (a) a sample inlet valve (**10**), which is connected to a syringe pump (**2**, 260D, ISCO, USA) with an internal volume about 266.03 cm^3, operable up to 51.7 MPa. With the aid of a controller (**3**) the uncertainty of volume reading is ± 0.01 cm^3; (b) the gas release valve (**13**) is connected to the vacuum and degassing unit. The cell has its own cooling circuit to allow cooling water running through the cell. The equilibrium cell was also modified by attaching a bottom drain valve A1777VB (**7**) provided by Parr Instrument Company to withdraw oligomeric solutions.

During the experiment, the pressure at equilibrium conditions was read to an uncertainty of ± 0.1 % by using a pressure transducer (PDCR-912, (0 to 15) bar, Druck, UK) with a digital display (**9**, DPI-280, Druck, UK) which was equipped to the cell as a modification of the original HP/HT reactor as well. A digital thermometer (**11**, K-type, TES Electrical Electronic Corp., Taiwan) was used to read the equilibrium temperature with an uncertainty of ± 0.1 K after calibration. The uncertainties of the reported temperature and pressure were estimated to be better than ± 0.2 K and ± 0.2 %, respectively, including the calibrated uncertainties and the fluctuation of temperature and pressure during the course of measurement.

Procedures. Initially, air and chemicals inside the cell were evacuated with a vacuum pump. The oligomeric materials and the solvents were separately degassed to remove the noncondensible dissolved gases. The degassed oligomer and the solvent were weighted by an electronic balance and then mixed well using a magnetic stirrer to prepare polymer solution at a specific composition (i.e., a pseudopure system). The uncertainty of the composition of the prepared solution is estimated to be ± 0.0001 in mass fraction. The mixed sample was stored in an Erlenmeyer flask (**4**) and loaded into an equilibrium cell using the syringe pump. The cell was regulated to a desired temperature and kept agitation. After system reached equilibrium state and stable pressure values were attained within an acceptable tolerance (± 1 kPa), the readings were recorded as equilibrium pressure (p) at the specific temperature (T). Since the volatility of the oligomer is substantially smaller than that of the organic solvents, the content in the vapor phase is assumed to be pure solvent only. The composition of liquid phase (x_i) was then calculated from the total composition of the loaded mixture with a minor correction of the solvent evaporating from liquid phase to vapor phase in the equilibrium cell. To minimize the amount of correction, the vapor space was kept as small as possible. Typically, the mass of the loaded mixtures is no less than 160 g. The uncertainty of the reported liquid composition is estimated as ± 0.001, including the correction of solvent evaporating. Another VLE measurement for the same loaded mixture at different temperatures was continuously made by changing the set point of cell's temperature. After a series of measurements for a given loaded mixture, the bottom drain valve was opened to withdraw the oligomeric solution from the cell. The nitrogen cylinder (**1**) was used for purging the equilibrium cell and for pressure testing as well.

■ RESULTS AND DISCUSSION

Experimental Results. To validate the experimental method for the VLE measurements with this apparatus, we first measured vapor pressures of pure solvent methanol at temperatures from (342.6 to 412.0) K; ethanol from (343.4 to 412.0) K; and propan-2-ol from (351.9 to 451.8) K. The experimental results

Table 1. Critical Properties and Parameters for the Wagner and the Tsonopoulos Equations[30]

solvent	T_c	$10^2\ p_c$	ω	Wagner parameters				Tsonopoulos parameters	
	K	kPa		c_1	c_2	c_3	c_4	a	b
methanol	512.64	80.92	0.565	−8.63571	1.17982	−2.4790	−1.0240	0.0878	0.0525
ethanol	513.92	61.32	0.649	−8.68587	1.17831	−4.8762	−1.5880	0.0878	0.0559
propan-2-ol	508.30	47.63	0.665	−8.73656	2.16240	−8.70785	4.77927	0.0878	0.0461

Table 2. Experimental Vapor Pressures for Methanol, Ethanol, and Propan-2-ol

methanol			ethanol			propan-2-ol		
T/K	p/kPa	$10^2\Delta p/p$[a]	T/K	p/kPa	$10^2\Delta p/p$[a]	T/K	p/kPa	$10^2\Delta p/p$[a]
342.6	121.5	−0.9	343.4	71.2	−0.7	351.9	88.3	+0.2
352.5	177.6	+0.5	351.1	98.0	−0.6	362.3	132.7	−0.1
363.3	258.1	+0.5	353.1	106.8	+0.1	372.6	194.9	+0.9
373.3	355.7	+0.1	362.1	151.0	+0.1	382.4	272.9	+1.1
382.3	465.3	−0.4	371.8	213.9	+0.4	393.6	386.7	+0.4
392.2	622.8	−0.0	372.4	218.1	+0.2	403.0	505.9	−0.5
393.2	640.0	−0.1	382.1	302.4	+0.3	413.0	664.6	−0.9
402.1	820.0	+0.2	393.0	424.1	−0.2	422.7	859.0	−0.1
412.0	1058.0	−0.1	402.3	557.9	−0.2	432.1	1085.5	+0.3
			412.0	733.0	+0.1	442.0	1359.9	+0.1
						451.8	1678.1	−0.1

[a] $\Delta p/p = [p - p(\text{calc.})]/p$, where $p(\text{calc.})$ is calculated from the Wagner equation, eq 1, with the parameters given in Table 1.

Table 3. Saturated Pressures of POEOPE (1) + Methanol (2)

$x_1 = 0.100$		$x_1 = 0.143$		$x_1 = 0.200$		$x_1 = 0.300$	
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
341.0	93.3	343.6	99.4	343.2	75.9	343.1	72.2
341.6	94.5	344.6	103.5	343.8	76.6	345.3	74.8
342.6	98.2	352.5	137.0	352.5	98.0	353.2	85.9
352.5	145.7	353.1	139.2	353.2	99.5	353.5	86.1
353.5	151.2	353.5	141.0	362.8	124.0	354.5	86.7
354.5	156.9	362.6	184.5	363.2	125.6	363.2	96.2
361.4	202.0	363.1	186.0	383.2	177.2	363.4	96.8
362.4	208.0	363.4	187.2	393.2	220.7	364.8	99.4
363.4	214.6	373.1	235.3			371.4	116.2
372.4	276.3	373.3	236.2			373.1	119.3
382.3	368.4	383.2	298.8			374.3	122.1
392.2	479.6	394.4	383.4			383.3	142.2
394.2	500.2	403.1	462.0			384.0	143.1

Table 4. Saturated Pressures of POEOPE (1) + Ethanol (2)

$x_1 = 0.100$		$x_1 = 0.200$		$x_1 = 0.300$	
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
345.1	74.5	342.6	61.1	343.2	54.1
353.0	92.3	343.1	61.9	343.6	54.6
353.1	92.4	353.1	82.9	344.3	55.9
353.5	93.5	353.8	84.5	353.0	70.0
363.1	132.0	361.2	98.1	354.1	71.9
373.1	179.4	363.1	100.8	363.1	87.9
373.2	179.9	363.4	101.7	364.1	89.4
373.3	180.4	364.8	105.3	365.4	91.2
373.7	181.9	370.9	126.8	372.9	108.7
381.4	232.4	373.1	133.0	373.8	109.4
383.1	244.4	373.2	133.4	374.1	110.5
383.2	245.5	373.3	134.3	383.2	131.5
393.0	317.1	383.2	172.2	384.0	134.3
402.4	407.8	384.3	175.8	385.5	136.3
404.6	431.8	393.2	215.2	402.5	178.6
413.0	516.4	403.2	261.2	403.2	181.7
413.1	517.4	404.1	265.9	413.6	218.1
414.5	537.4	405.1	269.0	423.2	250.1
423.2	670.9	413.3	326.5	423.3	251.9
423.9	681.5	414.0	329.5	432.9	288.0
434.3	864.7	423.0	400.2	433.4	286.7
444.3	1083.5	433.2	482.6	443.0	346.3
454.1	1322.6	443.3	585.4		
		452.9	709.4		

are compared with those calculated from the Wagner equation:[30]

$$\ln\left(\frac{p}{p_c}\right) = (1-\tau)^{-1}[c_1\tau + c_2\tau^{1.5} + c_3\tau^{2.5} + c_4\tau^5] \tag{1}$$

with

$$\tau = 1 - \frac{T}{T_c} \tag{2}$$

where T_c and p_c are the critical temperature and pressure, respectively. The critical properties and the parameters c_1 to c_4 of pure components are given in Table 1, and the relative deviations between the experimental data and the calculated values from eq 1 are reported in Table 2. It shows that the agreement is satisfactory.

The VLE apparatus was subsequently used in the VLE measurements for three binary systems of POEOPE with methanol, ethanol, and propan-2-ol at temperatures ranging from (341 to 454) K. Each binary system includes at least three loaded mixtures with specific compositions, and the mole fractions of POEOPE are up to 0.300. Tables 3 to 5 report the experimental results for these three binary systems. As an illustrative example, a semilog plot of saturated pressure varying with the reciprocal of temperature for the POEOPE + ethanol system is presented in Figure 2. An approximately linear relation is exhibited on this graph for each pseudopure system. A similar behavior was also observed from the other two investigated systems. The saturated pressure data of each pseudopure system were correlated with the Antoine equation:

$$\log_{10}(p/100) = A - \frac{B}{T + C - 273.15} \tag{3}$$

Table 5. Saturated Pressures of POEOPE (1) + Propan-2-ol (2)

$x_1 = 0.100$		$x_1 = 0.145$		$x_1 = 0.200$		$x_1 = 0.300$	
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
351.6	77.1	351.8	69.5	350.1	60.1	351.7	49.8
360.9	101.9	363.3	98.1	354.7	70.3	352.7	51.4
363.0	112.0	373.7	150.2	362.7	88.3	364.5	71.4
363.8	113.8	383.8	204.8	371.4	113.8	374.9	88.0
371.6	156.5	394.8	279.0	373.7	122.7	385.6	110.1
373.3	165.4	404.5	362.1	382.6	161.0	396.2	146.6
384.0	229.6	414.1	462.6	384.0	166.1	405.4	174.6
393.4	308.3	423.9	572.4	393.1	208.8	417.6	212.6
402.7	406.0	434.1	734.3	395.3	219.3	427.7	251.4
403.6	414.4	444.2	905.6	405.1	274.9	436.8	279.2
412.9	522.7	453.2	1082.7	406.1	277.9	442.0	310.9
414.2	532.9			415.0	348.4	451.4	380.2
422.9	680.0			415.4	349.7		
423.5	693.2			424.1	433.2		
433.2	873.8			425.7	443.7		
433.6	880.3			434.3	522.2		
442.6	1083.2			434.7	526.6		
442.8	1086.8			443.3	637.6		
451.6	1306.3			443.8	641.9		
				452.8	777.7		
				453.3	776.8		

Table 6. Correlation Results from the Antoine Equation

system[a]	x_1	T/K	Antoine constants[b]			$10^2\Delta p/p$[c]
			A	B	C	
M1	0.100	341.0−394.2	4.94273	1532.80	240.451	2.2
	0.143	343.6−403.1	4.48180	1539.93	274.580	2.0
	0.200	343.2−393.2	3.74694	1438.98	303.825	2.4
	0.300	343.1−384.0	3.52356	1693.5	390.286	2.5
M2	0.100	345.1−454.1	4.98305	1712.01	261.964	1.3
	0.200	342.5−452.9	5.46441	2729.41	411.093	1.3
	0.300	343.2−443.0	3.65807	1553.02	327.393	2.0
M3	0.100	351.6−451.6	4.95541	1560.71	228.739	7.0
	0.145	351.8−453.2	4.67918	1483.32	228.122	2.0
	0.200	350.1−453.3	4.50523	1593.10	260.254	1.0
	0.300	351.7−451.4	3.79156	1515.81	292.621	2.5
10^2 overall AARD[d]						2.4

[a] M1: POEOPE (1) + methanol (2); M2: POEOPE (1) + ethanol (2); M3: POEOPE (1) + propan-2-ol (2). [b] p in kPa and T in Kelvin. [c] $\Delta p/p = (1/n_p)\sum_{k=1}^{n_p}|p(\text{calc.})_k - p(\text{expt.})_k|/p(\text{expt.})_k$, where n_p is the number of data points. [d] Overall AARD $= (1/N)\sum_{k=1}^{N}|p(\text{calc.})_k - p(\text{expt.})_k|/p(\text{expt.})_k$, where N is the total number of data points of M1, M2, and M3.

Table 7. Structural Parameters Used in the UNIQUAC Model

molecule	r	q
methanol	1.431	1.432
ethanol	2.576	2.588
propan-2-ol	3.249	3.124
POEOPE	24.848	20.192

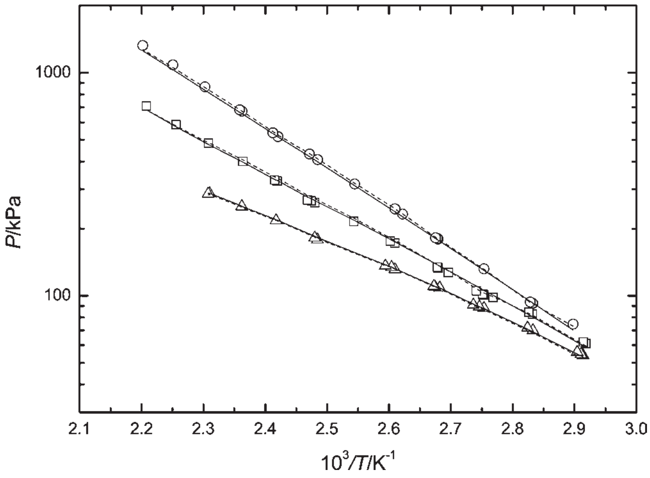

Figure 2. Saturated pressures of POEOPE (1) + ethanol (2): ○, x_1 = 0.100; □, x_1 = 0.200; △, x_1 = 0.300; —, UNIQUAC; ---, NRTL.

The determined Antoine constants, A, B, and C, for each pseudopure system, are reported in Table 6, indicating that the data fitting is reasonably well over the entire temperature range. The overall average absolute relative deviation (AARD) is 2.4 % for these three investigated systems.

Correlation with Activity Coefficient Models. In this study, two correlative activity coefficient models, the UNIQUAC and the NRTL models, were applied to correlate these new VLE data. The UNIQUAC model is widely used for highly nonideal systems since the combinatorial contribution of the equation is applicable to account for the large difference in molecular sizes between solvent and polymer, as demonstrated in the original paper for benzene + polyisobutylene and water + polyethylene glycol systems.[28] For the activity of solvent (2) in a binary polymeric solution system, the UNIQUAC equation is given by:

$$\ln a_2 = \ln \gamma_2^{\text{C}} + \ln \gamma_2^{\text{R}} + \ln x_2 \tag{4}$$

where superscripts C and R denote combinatorial and residual terms, respectively. The expressions of these two terms have been detailed in the original paper. The input variables of this model are the segment (or volume) parameter (r_i) and surface area parameter (q_i) for component i, respectively, which are listed in Table 7. For each binary system, there are four adjustable parameters, a_{ij}, a_{ji}, b_{ij}, and b_{ji} in the UNIQUAC model, which are defined as follows.

$$\tau_{ij} = \exp[-a_{ij} + (b_{ij}/T)] \tag{5}$$

$$\tau_{ji} = \exp[-a_{ji} + (b_{ji}/T)] \tag{6}$$

The optimal values of the binary parameters were determined from fitting the VLE data to the UNIQUAC model by minimization of the following objective function, π:

$$\pi = \sum_{k=1}^{n_p} [p(\text{calc.})_k - p(\text{expt.})_k]^2 \tag{7}$$

where n_p is the number of data points.

Alternatively, the NRTL equation is one of the widely used molecular thermodynamic expressions for the excess Gibbs

Table 8. Correlated Results from the UNIQUAC Model

system[a]	x_1	T/K	a_{12}	a_{21}	b_{12}/K	b_{21}/K	$10^2\Delta p/p$[b]
M1	0.1000	341.0−394.2	5.105	−6.525	−1670.1	1933.6	5.4
	0.1430	343.6−403.1					3.4
	0.2000	343.2−393.2					8.2
	0.3000	343.1−384.0					4.2
M2	0.1000	345.1−454.1	−0.287	3.093	−261.4	−962.1	2.1
	0.2000	342.5−452.9					2.6
	0.3000	343.2−443.0					0.9
M3	0.1000	351.6−451.6	−0.928	2.355	135.1	−730.8	5.4
	0.1450	351.8−453.2					5.5
	0.2000	350.1−453.3					1.3
	0.3000	351.7−451.4					5.0
10^2 overall AARD[c]							4.0

[a] M1: POEOPE (1) + methanol (2); M2: POEOPE (1) + ethanol (2); M3: POEOPE (1) + propan-2-ol (2). [b] $\Delta p/p = (1/n_p)\sum_{k=1}^{n_p}|p(\text{calc.})_k - p(\text{expt.})_k|/p(\text{expt.})_k$, where n_p is the number of data points. [c] Overall AARD = $(1/N)\sum_{k=1}^{N}|p(\text{calc.})_k - p(\text{expt.})_k|/p(\text{expt.})_k$, where N is the total number of data points of M1, M2, and M3.

Table 9. Correlated Results from the NRTL Model

system[a]	x_1	T/K	a_{12}	a_{21}	b_{12}/K	b_{21}/K	$10^2\Delta p/p$[b]
M1	0.1000	341.0−394.2	−10.839	−0.065	7589.1	−1058.2	0.9
	0.1430	343.6−403.1					2.2
	0.2000	343.2−393.2					9.4
	0.3000	343.1−384.0					9.6
M2	0.1000	345.1−454.1	3.966	−12.762	−8882.9	3707.8	0.9
	0.2000	342.5−452.9					2.6
	0.3000	343.2−443.0					1.4
M3	0.1000	351.6−451.6	22.805	0.009	10000.0	−1729.4	1.9
	0.1450	351.8−453.2					1.7
	0.2000	350.1−453.3					1.8
	0.3000	351.7−451.4					2.0
10^2 overall AARD[c]							3.1

[a] M1: POEOPE (1) + methanol (2); M2: POEOPE (1) + ethanol (2); M3: POEOPE (1) + propan-2-ol (2). [b] $\Delta p/p = (1/n_p)\sum_{k=1}^{n_p}|p(\text{calc.})_k - p(\text{expt.})_k|/p(\text{expt.})_k$, where n_p is the number of data points. [c] Overall AARD = $(1/N)\sum_{k=1}^{N}|p(\text{calc.})_k - p(\text{expt.})_k|/p(\text{expt.})_k$, where N is the total number of data points of M1, M2, and M3.

Table 10. Calculated Values of Solvent Activities for the Oligomeric Systems

system[a]	x_2	a_2				
		353.2 K	373.2 K	393.2 K	413.2 K	433.2 K
M1	0.700	0.474	0.346	0.266		
	0.800	0.562	0.448	0.370		
	0.857	0.770	0.681	0.613		
	0.900	0.824	0.810	0.801		
M2	0.700	0.663	0.486	0.378	0.309	0.263
	0.800	0.760	0.607	0.514	0.456	0.421
	0.900	0.889	0.808	0.756	0.723	0.704
M3	0.700	0.578	0.444	0.362	0.311	0.278
	0.800	0.724	0.625	0.563	0.525	0.503
	0.855	0.795	0.739	0.705	0.687	0.682
	0.900	0.861	0.824	0.806	0.803	0.810

[a] M1: POEOPE (1) + methanol (2); M2: POEOPE (1) + ethanol (2); M3: POEOPE (1) + propan-2-ol (2).

energy in the chemical industry today, especially for highly nonideal systems.[31] Particularly, the NRTL equation is a flexible local composition model that can be used for the correlation of phase equilibrium data and for representing complex VLE behavior in binary or multicomponent systems. For binary mixtures, the expression of activity coefficients using the NRTL model has been given by:

$$\ln \gamma_1 = {x_2}^2 \left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \left(\frac{\tau_{12} G_{12}}{(x_2 + x_1 G_{12})^2}\right)\right] \text{ and}$$

$$\ln \gamma_2 = x_1^2 \left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \left(\frac{\tau_{21} G_{21}}{(x_1 + x_2 G_{21})^2}\right)\right] \qquad (8)$$

For each binary system, there are also four adjustable parameters, a_{ij}, a_{ji}, b_{ij}, and b_{ji} which are defined as follows.

$$\tau_{ij} = a_{ij} + b_{ij}/T \qquad (9)$$

$$\tau_{ji} = a_{ji} + b_{ji}/T \qquad (10)$$

The nonrandomness factor, α_{ij}, is fixed to the value of 0.3 through the calculation. Optimal values of the UNIQUAC and the NRTL model parameters were determined on the basis of the modified Barker method principle[32] by minimization of the objective function, π, as defined in eq 7.

Tables 8 and 9 list the correlated results from the UNIQUAC and the NRTL models, respectively. As an example, Figure 2 shows the comparisons of experimental and correlation results for the POEOPE + ethanol system. In overall, the NRTL model was found to yield better results for correlating the $p-T-x$ data over a wide temperature range, with an overall AARD of 3.1 %, while that from the UNIQUAC model is 4.0 %.

Calculation of Solvent Activities. The solvent activities in the oligomeric systems were calculated from equating the fugacities of the solvent (component 2) in the vapor and the liquid phases. The oligomer can be considered as a nonvolatile component, thus assuming that the vapor phase is pure solvent and the fugacity in the vapor phase was calculated from the two-term virial equation. As a consequence, the activity of the solvent, a_2, was obtained from the following equation:[12,33]

$$a_2 = (p/p_2^0) \exp[-B_2(p_2^0 - p)/(RT)] \qquad (11)$$

where p is the equilibrium pressure and R is the gas constant. ${p_2}^0$ is the vapor pressure of the pure solvent at temperature T, calculated from the Wagner equation. B_2 is the second virial coefficient of the solvent, and the value at temperature T was estimated from the correlation of Tsonopoulos.[34] All of the constants used in the Tsonopoulos model, including the critical properties and the acentric factor of each solvent, are listed in Table 1. The solvent activities calculated from eq 11 are presented in Table 10 where the equilibrium pressures p at the specific temperatures were evaluated from the Antoine equation with the constants listed in Table 6. Figure 3 illustrates the effect of temperatures on the solvent activities of ethanol in POEOPE and the values of a_2 varying with the mole fraction of solvent. The results reveal that the solvent activities increase with increasing the solvent's mole fraction at a given temperature, while those decrease with increasing temperature at a given composition. As can be seen from the graph, this oligomeric system showed nonideal behavior. The activities of ethanol in POEOPE show

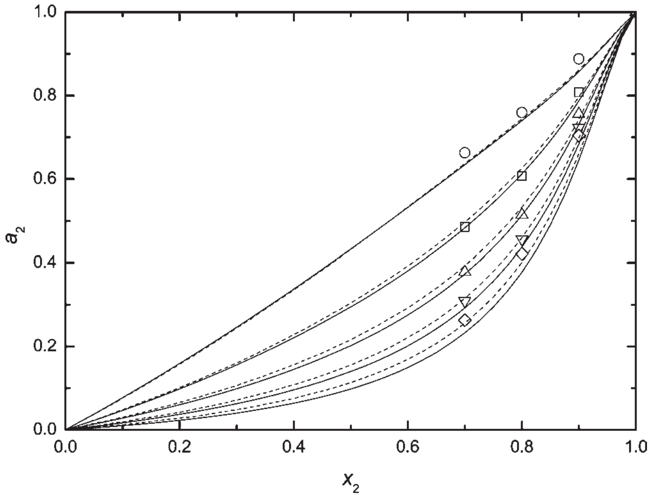

Figure 3. Activities of ethanol in POEOPE at various temperatures: ○, T = 353.2 K; □, T = 373.2 K; △, T = 393.2 K; ▽, T = 413.2 K; ◇, T = 433.2 K; —, UNIQUAC; ---, NRTL.

negative deviations and become larger deviations as the increase of temperatures. The graph is also shown that the activities calculated from the UNIQUAC and the NRTL models agree well with those from eq 11 and the NRTL model yielded slightly better results. A similar behavior was observed from the other investigated systems.

CONCLUSIONS

Vapor−liquid equilibrium data have been measured by using an autoclave VLE apparatus for three binary systems of POEOPE + methanol from (341.0 to 403.1) K, POEOPE + ethanol from (342.6 to 454.1) K, and POEOPE + propan-2-ol from (350.1 to 453.3) K. The saturated vapor pressure data of each binary system with a specific composition were fitted to the Antoine equation with an overall AARD of 2.4 %. The $p-T-x$ data were also correlated with two activity coefficient models, the UNIQUAC and the NRTL, respectively. For these three investigated oligomeric systems, the NRTL equation yielded better results with an overall AARD of 3.1 %. Significant deviations from ideal-solution behavior were found from these three oligomeric systems, when the smoothed saturation pressures were used to evaluate solvent activities at various temperatures. The calculated results of solvent activities from the NRTL model agree well with those evaluated from the experimental results.

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