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

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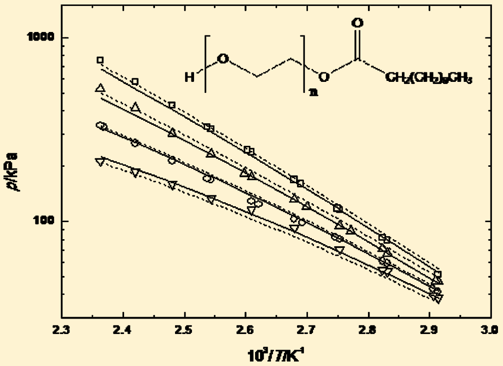
ABSTRACT: Isothermal vapor−liquid equilibrium (VLE) data have been measured for oligomeric polyoxyethylene dodecanoate (POEDDA) with methanol, ethanol, or propan-2-ol. A synthetic method was used to determine experimentally $p-T-x$ data in the temperature range of (343.2 to 423.2) K. For each binary system, four feed compositions were studied over the concentration range from 0.100 to 0.400 of POEDDA in mole fractions. These new VLE data were fitted to the Antoine equation and also correlated with the nonrandom two-liquid (NRTL) and the universal quasichemical activity coefficient (UNIQUAC) models. The results reveal that the performance of the UNIQUAC and the NRTL models are almost the same. The solvent activities were directly calculated from VLE data and compared to those calculated from the NRTL and the UNIQUAC models.



INTRODUCTION

Oligomers based on poly(ethylene glycols) (PEGs) are one of the most popular polymeric materials used in agriculture, biotechnology, food industries, and pharmaceutical industries.[1−8] These materials are ubiquitous, their presence ranging from liquids to low-melting solids, depending on their molecular weights. The factors that have led to the extensive use of these glycol ether oligomers are their outstanding properties, such as low toxicity and volatility, biodegradability, as well as excellent solubility in a variety of organic liquids.[9−14] Moreover, they are commercially available in a wide range of molecular weights and high purity and are, indeed, less expensive in comparison with several neoteric solvents such as ionic liquids (ILs).[15−18] Recently, PEGs have become the solvent of choice in the hydrogen sulfide removal process because of their good thermal and chemical stability and their ready availability at moderate cost.[19] In general, most PEGs are extremely effective in the coabsorption of hydrocarbons and dehydration of natural gases.[20]

For design and material processing for specific applications, it is necessary to understand the phase behavior of polymeric systems. Despite their significance in varied applications, however, the physical property database for PEGs is still modest in a number of systems and in the experimental conditions available. Furthermore, the specialized experimental references in the vapor−liquid equilibrium (VLE) of PEGs with alcohol mixtures are rather scarce. In addition to the VLE of polymer solution data collection by Wen et al.[21,22] and by Wohlfarth,[23] Zafarani-Moattar and co-workers[24−27] measured the solvent activities of PEG + methanol, PEG + ethanol, PEG + propan-2-ol, polyethylene glycol methacrylate (PEGMA) + methanol, PEGMA + ethanol, PEGMA + propan-2-ol, and PEGMA + 1-butanol by using the isopiestic method. It is notable that binary systems of PEG with methanol and ethanol have also been studied by Kim et al.[28] by using the electromicrobalance technique, at different alcohol compositions and polymer molecular weights. Other VLE data sources for PEGs with alcohol systems can be found in open literature.[29−33] Nevertheless, phase equilibrium studies for oligomeric glycol ethers with alcohols are still limited. It is thus extremely important to provide reliable VLE data of the relevant mixtures.

The present work is the continuation of a systematic study on VLE measurements of binary mixtures of oligomeric materials with alcohols. In our earlier works, an autoclave apparatus was employed to measure the saturated pressures for the binary mixtures of oligomer polyoxyethylene 4-octylphenyl ether (POEOPE) and polyethylene glycol mono-4-nonylphenyl ether (PEGNPE) with methanol, ethanol, and propan-2-ol.[34,35] In spite of the numerous advantages of this technique, such as reliable measurement within a wide range of temperature and pressure operation, simplicity, and ease of use, it is scarcely used for mixtures containing polymeric materials. In this study, the $p-T-x$ data of oligomeric polyoxyethylene dodecanoate (POEDDA) with methanol, ethanol, and propan-2-ol were measured at temperatures from (343.2 to 423.2) K. The selection of POEDDA for this study was made on the basis that this oligomer has diverse applications.[36] To our knowledge, to date no comparable data were found in the open literature for these three binary systems. Emphasis will be placed upon the applicability of the nonrandom two-liquid (NRTL)[37] and the

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universal quasichemical activity coefficient (UNIQUAC)[38] models for the VLE data correlation. The solvent activities were also calculated adopting the parameters obtained from those models and compared with the values directly evaluated from experimental results.

■ EXPERIMENTAL SECTION

Materials. The solvents used in the present study, including methanol, ethanol, and propan-2-ol, are analytical grade reagents purchased from Aldrich Chemical Co. (St. Louis, MO, USA). The purity levels of these compounds are better than 0.998 (mass fraction) which have been verified by gas chromatography (GC) analysis. Polyoxyethylene dodecanoate (POEDDA), CAS Registry No. 9004-81-3, with a number-average molecular weight (M_n) of 400 g·mol^{-1} and a polydispersity (M_w/M_n) of 1.043, was supplied by Tokyo Chemical Industry Co. (Japan). The molecular structure of this oligomer is shown in Scheme 1. All chemicals were used after degassing. Table 1 lists the materials description.

Scheme 1. Molecular Structure of POEDDA

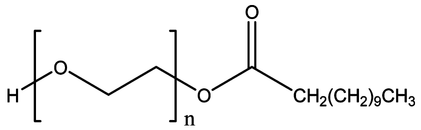

Table 1. Materials Description

substance	source	mass fraction purity	purification method
POEDDA	TCI, Japan		degas
methanol	Aldrich, USA	>0.998	degas
ethanol	Aldrich, USA	>0.998	degas
propan-2-ol	Aldrich, USA	>0.998	degas

Apparatus and Procedures. A synthetic method was used to determine experimentally saturated pressures of oligomeric POEDDA with alcohols. One characteristic of this method is that no sampling is required during the course of measurement. A modified Parr high pressure/high temperature reactor (model series 4576, T316 stainless steel, Parr Instrument Co., USA) was employed to obtain $p-T-x$ data in the temperature range of (343.2 to 423.2) K. The schematic diagram of the apparatus together with the experimental procedure has been given in our previous paper.[34,35] Briefly, it consists of an equilibrium cell (autoclave apparatus) with a 187 cm^3 maximum working capacity. Automatic temperature control was provided by the heater surrounding the cell and a cooling water system. The cell is connected to a controller series type 4843 (Parr Instrument Co., USA), which consists of a digital pressure display and a high temperature cutoff (J-type thermocouple) for safety purposes. Stirring was accomplished by a variable speed stirrer with a magnetic drive. Two valves are attached on the cell head: (a) a sample inlet valve which is connected to a syringe pump and (b) the gas release valve which is connected to a vacuum pump. Before loading liquid mixtures in the cell, it is necessary to vacuum the system thoroughly to evacuate the air and traces impurities inside the cell. To eliminate noncondensable gases, the oligomeric material and the solvent were separately subjected to a degassed procedure. The polymer solution was prepared gravimetrically with an electronic balance (model GR-200, A&D Scientech, Japan) to an uncertainty of ± 0.1 mg, and the oligomeric solution was introduced into the cell by using a syringe pump (260D, ISCO, USA). The temperature of the equilibrium cell was adjusted to a desired value, and stirring was continued. When equilibrium was attained, the pressure in the cell approached a constant value with an acceptable tolerance (± 1 kPa), and the reading was recorded. Generally, three hours were required for the system to reach equilibrium. The temperature of the cell was raised successively at 10 K intervals. During the experiment, the equilibrium temperature was measured with a digital thermometer (K-type, TES Electrical Electronic Corp., Taiwan) with an uncertainty of ± 0.1 K. A pressure transducer (PDCR-912, (0 to 15) bar, Druck, UK) with a digital display (DPI-280, Druck, UK) was used to read the saturated pressure with an uncertainty of ± 0.2 %, including the accuracy of calibrated uncertainty and the fluctuations of the pressure during the measurements. The uncertainty of the reported liquid composition was estimated as ± 0.001, including the correction of solvent evaporating. The bottom drain valve was used to withdraw the oligomeric solution after each series of runs. Nitrogen was further used for purging the cell.

■ RESULTS AND DISCUSSION

Preliminary experiments have been performed to verify the reliability of the VLE apparatus and its operation. The vapor pressures of methanol, ethanol, and propan-2-ol have been measured[34] and compared with the calculated values from the Wagner equation.[39] The experiments have been carried out in the temperature range of (342.6 to 451.8) K, and the comparison showed that the agreement is satisfactory, to within ± 0.3 %.

New $p-T-x$ data were measured for the mixtures of POEDDA with the alcohols by using the VLE apparatus. The investigated systems were POEDDA + methanol, POEDDA + ethanol, and POEDDA + propan-2-ol. Four feed compositions were studied over the concentration ranging from 0.100 to 0.400 of POEDDA in mole fraction (x_1). The samples with higher concentrations of POEDDA could not be studied due to the difficulties in handling the highly viscous samples. Because the volatility of the oligomer is substantially lower than that of the organic solvents, the content in the vapor phase is reasonably assumed to be pure solvent.[40−42] The actual liquid composition (x_i) was corrected, taking into account the amount of the alcohols vaporized to the vapor phase. Since the volumes of the equilibrium cell and the charged solution are already known, the amount of pure alcohol presents in the vapor phase was estimated from the volume of the vapor phase and the equilibrium conditions. To minimize the amount of correction, we kept the vapor space as small as possible; that is, the loaded mixture is no less than 160 g. Under these circumstances, the uncertainty of the reported x_i was estimated to be less than ± 0.001.

The saturated pressure data given in Tables 2 to 4 were found to be well-represented by the Antoine equation:

$$\log_{10}(p/100) = A - \frac{B}{T + C - 273.15} \tag{1}$$

where p is saturated pressure in kPa, T is equilibrium temperature in K, and A, B, and C are Antoine constants. The nonlinear correlation procedure, with the Levenberg−Marquardt (LM) algorithm,[43] was used to determine the best fit values of the Antoine constants for each binary system with a

Table 2. Saturated Pressures of POEDDA (1) + Methanol (2)[a]

x_1 = 0.100		x_1 = 0.150		x_1 = 0.200		x_1 = 0.250	
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
343.2	102.0	343.2	90.4	343.2	84.2	343.2	70.8
353.2	145.5	353.2	124.5	343.6	85.0	344.2	72.7
354.1	149.4	363.2	167.2	352.5	110.5	350.6	88.4
362.2	192.7	372.4	205.9	353.2	111.5	353.2	92.6
363.2	200.1	373.2	209.3	355.6	117.9	354.2	95.3
372.2	259.5	374.2	214.8	361.8	142.2	363.2	118.6
373.2	265.5	375.2	220.7	363.2	143.0	372.4	146.9
374.3	274.8	383.2	259.5	365.2	154.1	372.4	146.9
383.2	345.3	384.1	268.0	373.2	175.3	373.2	147.5
393.2	462.3	393.2	335.4	374.2	183.8	383.2	175.4
395.1	487.8	403.2	452.3	382.7	222.9	393.2	204.3
403.0	603.8	413.2	575.5	383.2	227.5	403.2	234.2
403.2	606.7	423.2	739.3	392.8	292.3	413.2	267.6
403.2	607.8			393.2	293.5	423.2	297.5
412.3	770.9			394.5	303.5		
412.9	793.9			403.2	365.1		
413.2	801.1			413.2	403.5		
422.6	1012.3			423.0	510.6		
423.2	1041.5			423.2	513.7		

[a] $u(x_1) = 0.001$; $u(T) = 0.1$ K; $u(P) = 0.2$ %.

Table 3. Saturated Pressures of POEDDA (1) + Ethanol (2)[a]

x_1 = 0.100		x_1 = 0.200		x_1 = 0.300		x_1 = 0.400	
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
343.2	61.0	343.2	54.0	343.2	53.1	343.2	42.0
345.2	66.1	344.2	56.2	344.2	54.6	353.2	57.2
352.0	81.5	353.2	79.5	351.2	69.7	354.2	58.2
353.2	85.7	354.2	81.6	353.2	73.4	363.2	72.6
354.2	88.0	355.2	84.0	362.7	96.0	373.2	87.5
363.2	119.8	363.2	106.7	363.2	97.4	383.2	101.1
365.1	127.5	364.1	110.1	373.2	118.7	393.2	129.6
373.2	167.8	365.0	112.4	374.2	122.5	394.5	130.7
375.2	178.9	365.1	113.1	376.5	127.0	403.2	152.1
383.2	227.5	372.2	141.7	381.3	146.9	404.5	153.8
384.9	239.0	373.2	145.1	382.2	149.2	409.6	167.6
393.2	307.9	374.2	149.5	383.2	151.8	413.2	175.6
403.2	399.6	382.2	192.7	393.2	187.6	423.2	201.8
413.2	537.8	383.2	198.0	394.1	192.2		
422.3	676.2	384.2	203.7	403.2	230.5		
423.2	693.0	393.2	273.8	403.6	232.8		
		394.1	281.0	411.2	265.0		
		403.2	357.9	413.2	275.5		
		404.1	368.8	423.2	329.0		
		405.0	376.8				
		413.2	473.7				
		422.3	586.3				
		423.2	595.8				

[a] $u(x_1) = 0.001$; $u(T) = 0.1$ K; $u(P) = 0.2$ %.

Table 4. Saturated Pressures of POEDDA (1) + Propan-2-ol (2)[a]

x_1 = 0.100		x_1 = 0.200		x_1 = 0.300		x_1 = 0.400	
T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
343.2	51.5	343.2	47.0	343.2	41.2	343.2	38.4
353.2	78.8	343.6	47.4	344.2	42.8	344.2	39.5
354.2	81.5	353.2	67.0	353.2	59.2	353.2	53.4
363.2	115.8	354.2	70.9	354.2	60.8	354.2	54.5
363.7	118.0	360.8	88.8	363.2	80.0	363.2	70.4
371.8	160.2	363.2	94.9	364.1	81.9	373.2	92.2
373.2	168.6	370.4	120.7	371.4	98.3	383.2	115.4
383.2	238.4	373.2	132.3	373.2	102.6	393.2	133.3
384.2	245.0	383.2	174.8	381.6	124.1	403.2	159.3
393.2	318.0	384.9	182.2	383.2	128.5	413.2	186.3
394.1	327.2	393.2	232.6	393.2	167.8	423.2	213.0
403.2	428.0	403.2	300.6	394.1	171.0		
413.2	576.2	413.2	415.8	403.2	213.2		
423.2	752.8	423.2	526.8	413.2	266.7		
				422.3	325.8		
				423.2	332.2		

[a] $u(x_1) = 0.001$; $u(T) = 0.1$ K; $u(P) = 0.2$ %.

given concentration. The initial approximation for Antoine constants was taken from the Antoine constants for the pure solvents.[39] Table 5 summarized the adjusted constants of the Antoine equation together with their average absolute relative deviation (AARD) for each data set, with an overall AARD of 1.3 %.

The variations of saturated pressure with temperature at different oligomer concentrations are shown in Figures 1 to 3 for the systems containing methanol, ethanol, and propan-2-ol, respectively. From these graphs, the logarithm of pressure against the reciprocal temperature for a given oligomer composition is almost linear over the entire experimental range of pressure and temperature.

Correlation with Activity Coefficient Models. The UNIQUAC[37] and the NRTL[38] models were comparatively used for the correlation of the VLE data. These two models, together with the Wilson equation, are the most well-known and widely used in industrial applications.[44] Their excess Gibbs function (g^E) expressions accurately represent the nonidealities of most binary mixtures.[45] Moreover, these models require only a small number of adjustable parameters, together with structural parameters that commonly available in literature. The validity of these models for correlating the VLE data of systems containing polymeric components has been evidenced elsewhere.[21−23]

Omitting details, the UNIQUAC model for the activity coefficient of component i is expressed as:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{2}$$

where superscripts C and R were defined as combinatorial and residual terms, respectively. The compound-specific parameters in the UNIQUAC model represent the size and shape of the molecules and their interactions with one another. The values of the volume parameter (r) and the surface area parameter (q), which are needed in the calculation, are listed in Table 6. For oligomeric POEDDA, the values of the structural parameter r and q were estimated according to the method of Bondi.[46] The UNIQUAC interaction parameters defined by a linear function of temperature were used:

$$\tau_{ij} = \exp[-a_{ij} + (b_{ij}/T)] \tag{3}$$

where a_{12}, a_{21}, b_{12}, and b_{21} are temperature-independent constants.

The NRTL model has three parameters, that is, two binary interaction parameters (τ_{ij}) and the so-called nonrandomness factor (α_{ij}), which was fixed to 0.3 in the regression. For a binary system, the expressions of the activity coefficients of the

Table 5. Correlation Results for the Antoine Equation

system[a]	x_1	T/K	Antoine constants[b] A	B	C	$10^2\Delta p/p$[c]
M1	0.100	343.2−423.2	1.49109	211.094	58.905	1.2
	0.150	343.2−423.2	3.61792	1096.951	227.035	2.2
	0.200	343.2−423.2	6.78193	3619.297	460.234	1.9
	0.250	343.2−423.2	6.56988	2930.293	376.707	1.1
M2	0.100	343.2−423.2	6.14048	2539.527	329.092	0.8
	0.200	343.2−423.2	6.27316	2734.368	348.001	1.3
	0.300	343.2−423.2	2.89209	768.797	173.597	1.2
	0.400	343.2−423.2	1.76707	373.726	104.953	1.6
M3	0.100	343.2−423.2	4.67465	1299.402	191.805	0.7
	0.200	343.2−423.2	5.72213	2324.170	314.414	1.5
	0.300	343.2−423.2	3.92081	1311.497	235.112	1.7
	0.400	343.2−423.2	1.39489	208.410	44.968	0.9
10^2 overall AARD[d]						1.3

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

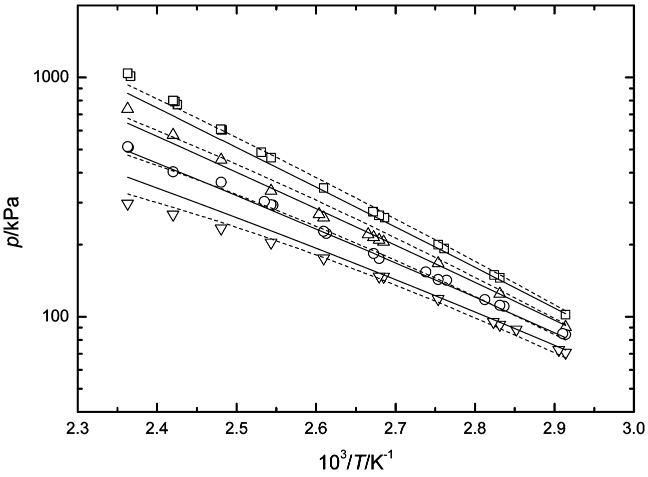

Figure 1. Saturated pressures of POEDDA (1) + methanol (2): □, $x_1 = 0.100$; △, $x_1 = 0.150$; ○, $x_1 = 0.200$; ▽, $x_1 = 0.250$; —, UNIQUAC; ---, NRTL.

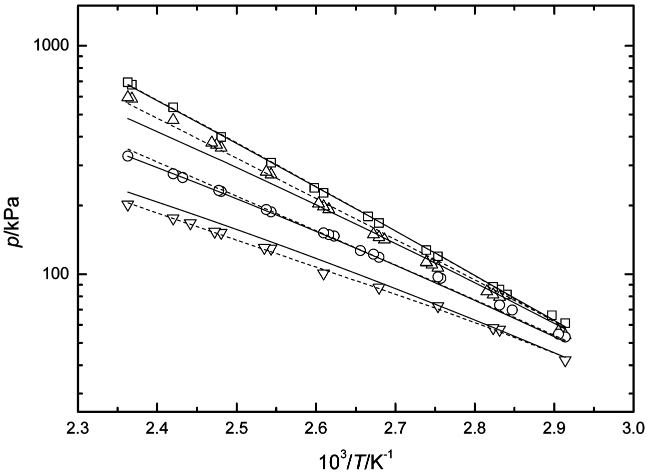

Figure 2. Saturated pressures of POEDDA (1) + ethanol (2): □, $x_1 = 0.100$; △, $x_1 = 0.200$; ○, $x_1 = 0.300$; ▽, $x_1 = 0.400$; —, UNIQUAC; ---, NRTL.

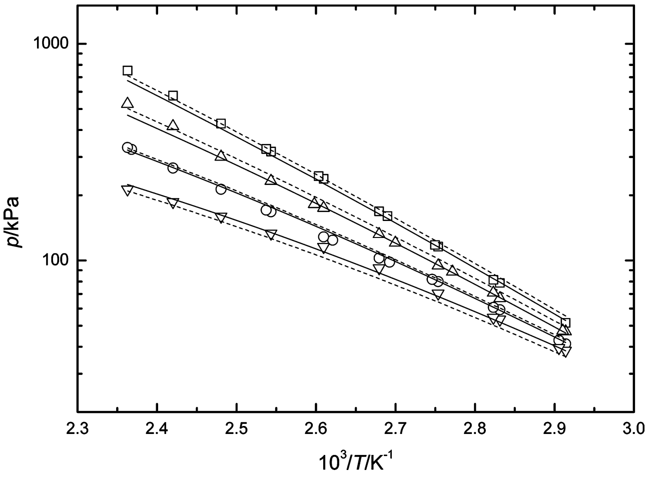

Figure 3. Saturated pressures of POEDDA (1) + propan-2-ol (2): □, $x_1 = 0.100$; △, $x_1 = 0.200$; ○, $x_1 = 0.300$; ▽, $x_1 = 0.400$; —, UNIQUAC; ---, NRTL.

Table 6. Structural Parameters Used in the UNIQUAC Model

compound	r	q
methanol	1.431	1.432
ethanol	2.576	2.588
propan-2-ol	3.249	3.124
POEDDA	20.052	16.712

constituent components are given as

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \left(\frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right)\right] \tag{4}$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \left(\frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right)\right] \tag{5}$$

with

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{6}$$

Table 7. 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	0.100	343.2−423.2	−0.502	3.437	−86.998	−1100.755	7.4
	0.150	343.2−423.2					3.9
	0.200	343.2−423.2					3.1
	0.250	343.2−423.2					7.5
M2	0.100	343.2−423.2	1.789	1.388	−937.619	−374.990	1.7
	0.200	343.2−423.2					6.9
	0.300	343.2−423.2					2.7
	0.400	343.2−423.2					7.2
M3	0.100	343.2−423.2	1.668	1.446	−1064.166	−298.346	3.7
	0.200	343.2−423.2					2.2
	0.300	343.2−423.2					2.9
	0.400	343.2−423.2					2.7
10^2 overall AARD[c]							4.3

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

Table 8. 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	0.100	343.2−423.2	−12.031	15.298	3409.701	−10000.000	4.1
	0.150	343.2−423.2					7.9
	0.200	343.2−423.2					3.5
	0.250	343.2−423.2					4.4
M2	0.100	343.2−423.2	−6.410	−18.832	1667.316	7322.758	1.9
	0.200	343.2−423.2					5.4
	0.300	343.2−423.2					3.2
	0.400	343.2−423.2					2.0
M3	0.100	343.2−423.2	−7.868	−8.118	2185.527	3560.544	3.3
	0.200	343.2−423.2					6.1
	0.300	343.2−423.2					4.5
	0.400	343.2−423.2					6.7
10^2 overall AARD[c]	4.4						

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

The binary parameters of the NRTL model, τ_{ij}, can be expressed in terms of temperature as:

$$\tau_{ij} = a_{ij} + b_{ij}/T \tag{7}$$

Similarly, four adjustable parameters, a_{12}, a_{21}, b_{12}, and b_{21}, for each binary system were determined from the VLE data correlation.

The experimental $p-T-x$ data reductions were made by means of the modified Barker method.[47,48] During the calculation, the optimal values of temperature-dependent parameters for each system were determined based on the Britt−Luecke algorithm[49] by the minimization of the following objective function, π:

$$\pi = \sum_{k=1}^{n_p}(p_k^{\text{calc}} - p_k^{\text{expt}})^2 \tag{8}$$

where n_p is the number of data points and the superscripts calc and expt refer to the calculated and experimental values, respectively.

The optimized parameters obtained from the UNIQUAC and the NRTL models are listed in Tables 7 and 8, respectively, along with the corresponding AARD of the best fit. According to the values of the overall AARD, it is indicated that the performance of the UNIQUAC model (4.3 %) is almost the same with the NRTL model (4.4 %). Graphical representations of the binary VLE data along with the calculated values using the UNIQUAC and the NRTL are illustrated in Figures 1 to 3 for systems containing methanol, ethanol, and propan-2-ol, respectively. As can be observed from the given figures, the agreement is satisfactory.

Solvent Activities Calculation. The deviations from ideal solution behavior can be reflected by the solvent activities calculation. The saturated pressure data obtained were directly used to calculate solvent activities. To obtain a relation between the solvent activities to the VLE data, the isofugacity criterion of the solvent component in both the vapor and the liquid phases was adopted. In this relationship, the oligomer was assumed to have negligible vapor pressures. For binary polymer solutions, the solvent activities can be expressed as:[21,50]

$$a_2 = (p/p_2^0)\exp[-B_2(p_2^0 - p)/(RT)] \tag{9}$$

Table 9. Calculated Values of Solvent Activities for the Oligomeric Systems

		a_2								
system[a]	x_2	343.2 K	353.2 K	363.2 K	373.2 K	383.2 K	393.2 K	403.2 K	413.2 K	423.2 K
M1	0.900	0.819	0.810	0.792	0.761	0.733	0.738	0.740	0.745	0.771
	0.850	0.728	0.696	0.666	0.606	0.558	0.544	0.561	0.555	0.562
	0.800	0.680	0.625	0.572	0.510	0.491	0.479	0.457	0.395	0.398
	0.750	0.574	0.522	0.477	0.431	0.382	0.337	0.298	0.266	0.235
M2	0.900	0.862	0.805	0.773	0.759	0.740	0.736	0.717	0.733	0.732
	0.800	0.765	0.749	0.691	0.659	0.648	0.659	0.646	0.651	0.637
	0.700	0.752	0.693	0.632	0.543	0.502	0.458	0.425	0.389	0.364
	0.600	0.598	0.543	0.474	0.403	0.338	0.320	0.284	0.252	0.226
M3	0.900	0.850	0.853	0.850	0.859	0.867	0.847	0.851	0.868	0.878
	0.800	0.777	0.728	0.701	0.681	0.645	0.630	0.611	0.643	0.634
	0.700	0.683	0.645	0.594	0.532	0.479	0.460	0.440	0.422	0.411
	0.600	0.637	0.583	0.524	0.479	0.432	0.368	0.332	0.298	0.268

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

where p is the equilibrium pressure and R is the gas constant. p_2° denotes the vapor pressure of pure solvent at temperature T, which was calculated from the Wagner equation. In the calculation, the nonideality behavior of the solvents was taken into account by using the two-term virial equation. The value of the second virial coefficient, B_2, was estimated from the Tsonopoulos correlation.[51] The values of the physical properties needed for the calculation of the Wagner and the Tsonopoulos equations were taken from Poling et al.[39] The calculated solvent activities (a_2) over the experimental temperature range were tabulated in Table 9.

Figures 4 to 6 illustrate the solvent activities varying with the solvent mole fraction. As can be seen from the graphs, all of these three systems showed nonideal behavior over the whole composition range. In general, the solvent activities increase with increasing the mole fraction of solvent at a given temperature and decrease with increasing temperature at a given composition. The agreement between the calculated solvent activities from eq 9 and those estimated from the UNIQUAC and the NRTL models is satisfactory.

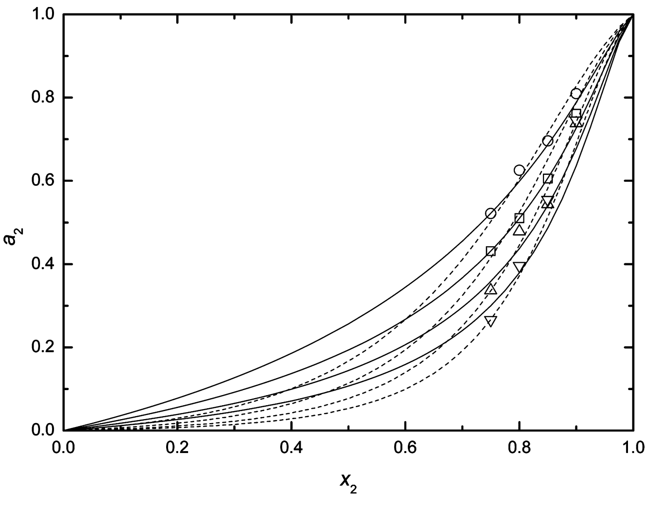

Figure 4. Activities of methanol in POEDDA at various temperatures: ○, T = 353.2 K; □, T = 373.2 K; △, T = 393.2 K; ▽, T = 413.2 K; —, UNIQUAC; ---, NRTL.

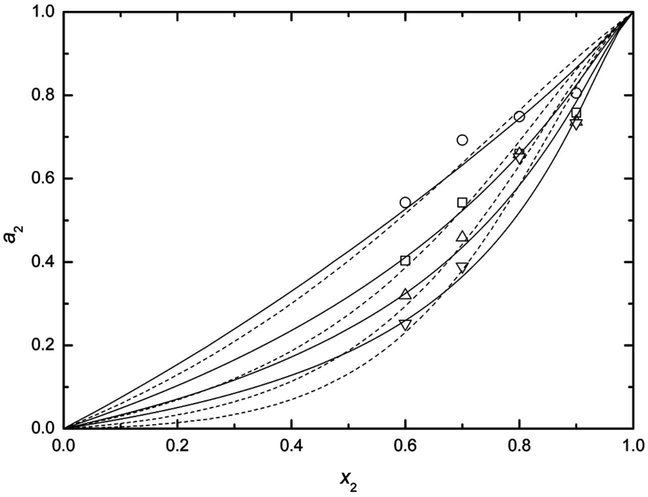

Figure 5. Activities of ethanol in POEDDA at various temperatures: ○, T = 353.2 K; □, T = 373.2 K; △, T = 393.2 K; ▽, T = 413.2 K; —, UNIQUAC; ---, NRTL.

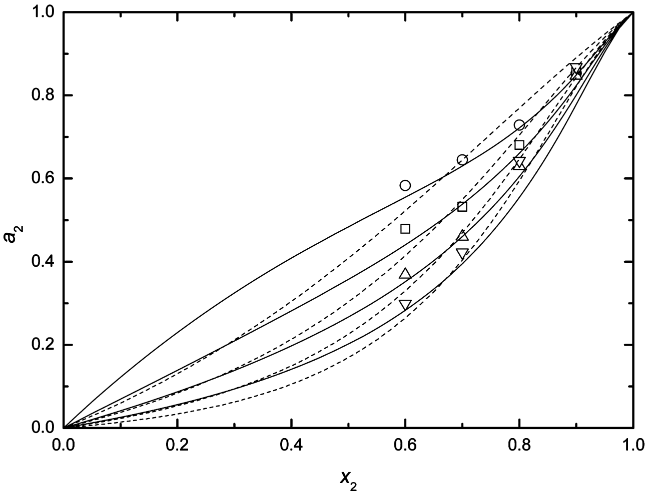

Figure 6. Activities of propan-2-ol in POEDDA at various temperatures: ○, T = 353.2 K; □, T = 373.2 K; △, T = 393.2 K; ▽, T = 413.2 K; —, UNIQUAC; ---, NRTL.

■ CONCLUSIONS

The present work measured the saturated pressures for three binary systems of POEDDA with methanol, ethanol, or propan-2-ol in the temperature range of (343.2 to 423.2) K. An autoclave apparatus was employed to measure the new $p-T-x$ data, including four feed oligomer compositions for each system. The VLE data of each binary system were correlated with the Antoine equation to an overall AARD of 1.3 %. The experimental results were compared with the correlated values from the UNIQUAC and the NRTL models as well. The performance of both models is almost the same, with an overall AARD of 4.3 % for the UNIQUAC model and 4.4 % for the NRTL models, respectively. The solvent activities calculated from these two solution models agreed well with those evaluated from the experimental results.

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