

Measurement and Correlation of Saturated Vapor Pressure of Ethylphenyldimethoxysilane and Ethylphenyldiethoxysilane

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Supporting Information

ABSTRACT: The saturated temperatures of ethylphenyldimethoxysilane (EPDMOS) and ethylphenyldiethoxysilane (EPDEOS) were determined using an inclined ebulliometer from 2.035 to 64.0 kPa. The experimental data were fitted with the Antoine and Clarke–Glew equations by a weighted least-squares regression method, which yielded Antoine parameters (A = 9.1280, B = 1590.18, C = -100.39 K and A = 9.1049, B = 1678.64, C = -102.84 K) and standard vaporization enthalpies ($\Delta_1^g H_m^0$ (298.15 K) = 62.52 kJ·mol⁻¹ and $\Delta_1^g H_m^0$ (298.15 K) = 65.19 kJ·mol⁻¹) for EPDMOS and EPDEOS, respectively. The critical properties of EPDMOS and EPDEOS, such as critical temperature, pressure, and volume, were estimated by the group contribution method introduced by Nannoolal et al. The acentric factors of EPDMOS and EPDEOS were estimated from these critical parameters and the reduced saturated vapor pressures calculated from either the Clarke–Glew equation or the Antoine equation.



1. INTRODUCTION

With rapid developments in space technology, an increasing number of requirements have been raised for rubber products and components for use in outer space. In such environments, rubber products need to maintain their flexibility and sealing performance at ultralow temperatures, and withstand frequent impact resistance at high and low temperatures, ultraviolet (UV) irradiation, and the impact of vacuum particles. Only special silicone rubber can meet these requirements under such stringent conditions. Rubber products can exhibit high flexibility at room temperature; however, they lose elasticity at lower temperature because of decreases in rubber molecular thermal motion and freezing of molecular chains. Two significant characteristics that affect the cold resistance of rubber are the glass phase and crystal transitions. The glass phase transition temperature (T_g) of silicone rubber is determined mainly by properties of the side organic groups attached to Si atoms in polysiloxane molecules, especially their amount, volume, and cohesive energy.¹ When the phenyl group is introduced into the side group of the Si atom in the polysiloxane backbone, the regularity of the polysiloxane backbone is destroyed and crystallization conducted at approximately -50 °C is inhibited extensively. Therefore, phenyl-group-modified silicone rubber exhibits better cold resistance. The regularity of the polysiloxane backbone could also be destroyed when the side methyl group is substituted partially by an ethyl group. With the introduction of an ethyl group, the crystallization process occurring at lower temperature is inhibited significantly, and thus, ethyl-modified silicone rubber manifests much better cold resistance than phenyl silicone rubber.² When aryl or polar-substituted groups are

introduced into the polysiloxane molecules, the rigidity of the polysiloxane molecule increases with a decrease in flexibility. The T_g value of the copolymer increases proportionally with content of modified units.³⁻⁶ The T_g of polydiethylsiloxane is as low as -145 °C.^{7,8} Its cold resistance is the most prominent among polysiloxanes, and thus, they show broad application prospects.^{9,10} The function of the phenyl group attached to the side chain of polysiloxane is not only to inhibit low-temperature crystallization but also to improve the thermal and UV resistance of silicone materials, together with a significant increase in their refractive index. Consequently, phenylmodified silicone materials are used extensively to encapsulate high-brightness light-emitting diode chips. In short, ethyl group-modified silicone polymers exhibit a cold resistance, whereas phenyl-containing silicone polymers possess excellent thermal and UV resistance. Because of the enormous structure and ring-opening polymerization rate differences between diethylsiloxane, diphenylsiloxane, and methylphenylsiloxane units, poly(diethyl-methylphenyl)siloxane or poly(diethyldiphenyl)siloxane copolymers with uniform structure and excellent performance are difficult to prepare.

Polysiloxane copolymers contain phenyl and ethyl groups in the side chains of repeating Si-O-Si segments could be prepared by ring-opening copolymerization with difunctional silane compounds containing diethyl and diphenyl or the methylphenyl group. When a difunctional silane compound that contains an ethyl and phenyl group is used as the

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Scheme 1. Schematic Diagram for EPDMOS Synthesis



Scheme 2. Schematic Diagram for EPDEOS Synthesis



Table 1. Sample Description

chemical name	CAS registry number	source	initial mass fraction purity	purification method	final mass fraction purity	analysis method	
EPDMOS ^b	112123-25-8	synthesis	0.568	distillation	0.9967	GC ^a	
EPDEOS ^c	16522-50-2	synthesis	0.557	distillation	0.9985	GC ^a	
^{<i>a</i>} Gas-liquid chromatography. ^{<i>b</i>} EPDMOS = ethylphenyldimethoxysilane. ^{<i>c</i>} EPDEOS = ethylphenyldiethoxysilane.							

polymeric monomer, the copolymers mentioned above can also be prepared. Compared with the former, the latter exhibit more advantages because the irregularity of the copolymer structure that arises from differences in the polymeric rate of two or more kinds of monomers can be avoided substantially. On the basis of such considerations, high purity ethyltrialkoxysilane compounds were synthesized and separated by Ru-catalyzed hydrosilylation initiated from trialkoxysilane and gaseous ethylene in our previous work.^{11,12} Ethylphenyldialkoxysilanes can be prepared by the Wurtz–Fittig reaction that occurs between ethyltrialkoxysilane and chlorobenzene.¹³

Although ethylphenyldimethoxysilane (EPDMOS, CAS RN: 112123-25-8, EPDMOS) and ethylphenyldiethoxysilane (EP-DEOS, CAS RN: 16522-50-2, EPDEOS) have been synthesized, some important experimental data, such as their density, normal boiling point, enthalpy of evaporation, and flash point, have never been reported in the literature. In the Chemical Abstracts Service database, only predicted results of parameters calculated from Advanced Chemistry Development (ACD) software have been provided.¹⁴ A comparison of experimental data and predicted results given by ACD software indicates that significant differences exist for other high boiling point chemicals. For example, the experimental normal boiling point of dimethylphenylethoxysilane (CAS RN: 1825-58-7) is in the range (195 to 196) °C,¹⁵ whereas the predicted result given by ACD software is 209.0 \pm 9.0 °C.¹⁴ The accuracy of predicted results for high boiling point chemicals therefore is difficult to guarantee.

To supplement fundamental data in silicone chemistry and to provide detailed parameters for industrial applications, values of saturation temperature at different pressures for EPDMOS and EPDEOS were measured using an inclined ebulliometer. The Antoine and Clarke–Glew equations were fitted to the experimental data and gave the Antoine parameters *A*, *B*, and *C*, standard vaporization enthalpy $\Delta_{\rm f}^{\rm g} H^0_m(\theta)$, standard Gibbs energy $\Delta_{\rm f}^{\rm g} G^0_m(\theta)$, and difference between the heat capacities of the ideal gas and liquid phase $\Delta_{\rm f}^{\rm g} C^0_{p,m}(\theta)$. The critical properties of EPDMOS and EPDEOS, including the critical temperature, pressure, and volume, were estimated using the group contribution method introduced by Nannoolal et al.²¹ The acentric factors of EPDMOS and EPDEOS were estimated using their respective critical parameters and their saturated vapor pressures calculated using either the Clarke-Glew equation or the Antoine equation.

2. EXPERIMENTAL SECTION

2.1. Chemicals. EPDMOS and EPDEOS were synthesized by the Wurtz-Fittig method as shown in Schemes 1 and 2.¹³ Synthetic crude products were separated and purified by vacuum distillation in a 1 m column of 30 mm inner diameter filled with Dixon θ packings (3 mm outer diameter, 3 mm length). The temperature at the top of the vacuum distillation tower was measured with a standard platinum resistance thermometer Pt-100 connected to an artificial intelligence industrial controller (AI-708 model, China Xiamen Yudian Automation Technology Co., Ltd.), and the absolute pressure in this distillation system was monitored by an Anschutz vacuum gauge (AM-1 type, China Shanghai Xingzhi Instrument Factory) with measurement range ranging from 0.027 kPa to 26.664 kPa. After removal of the low boiling point impurities and the front cut fractions, EPDMOS and EPDEOS were collected from the top of the distillation tower at 59.1 $^{\circ}C/0.23$ kPa and 84 °C/0.23 kPa, respectively. The standard uncertainty in temperature is u(T) = 0.2 K and the relative standard uncertainty in pressure is $u_r(p) = 10$ %.

The purity of the EPDMOS and EPDEOS was determined using a Rainbow gas chromatograph (GC) SP-6890 equipped with a flame ionization detector (Rainbow Chemical Instrument Co. Ltd., Shandong Lunan). A capillary column HP-5 (stationary phase cross-linked 5 % phenyl methyl silicone) was used with a column length of 25 m, inner diameter of 0.32 mm, and film thickness of 0.25 mm. The GC vaporizer and detector temperatures were set to T = 533 K. The standard GC column temperature program was started from T = 333 K followed by a heating rate of 0.167 K·s⁻¹ to T = 533 K. Samples used for vapor pressure measurements were detected with a mass fraction of 0.9967 and 0.9985 for EPDMOS and EPDEOS, respectively, and the results are listed in Table 1.

2.2. Vapor Pressure Measurement for EPDMOS and EPDEOS. The apparatus used in this work has been described previously¹⁶ and includes a high-accuracy pressure controller and measurement system, an inclined ebulliometer, and a vacuum pump (ILMVAC, Model P6Z). The system pressures were controlled by a DPI 515 precision pressure controller. The measurement stability of the pressure controller was 0.02 kPa

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up to 200 kPa with a control stability of 0.002 kPa. The relative standard uncertainty in pressure measurement was $u_r(p) = 2$ %. The temperature was measured with a standard platinum resistance thermometer Pt-100 connected to an artificial intelligence industrial controller (AI-526P model, China Xiamen Yudian Automation Technology Co., Ltd.). Temperature data were collected every 0.1 s by a computer through an RS-485/RS-232 converter and the uncertainty of the temperature measurement was 0.02 K.

The reliability and accuracy of the apparatus setup was verified during our previous work by measuring and comparing the saturation temperatures of *N*-methyl-2-pyrrolidone from 4.742 kPa to 99.402 kPa with those reported in the literature.¹⁷ The maximum absolute error of the apparatus was 0.13 K and the maximum relative difference was 0.034 %.

Samples of EPDMOS or EPDEOS with an approximate volume of 100 cm³ were loaded into the inclined ebulliometer. All measurements were conducted in sequence with increasing pressure which was controlled at the desired value for each experimental point. Samples were heated and stirred using a magnetic stirrer to provide isothermal conditions and to prevent superheating. When thermal equilibrium was reached, the temperature and pressure were recorded. Experimental temperatures were measured in triplicate at each pressure. The recorded saturation temperatures and corresponding vapor pressures are listed in Table 2.

3. RESULTS AND DISCUSSION

3.1. Regression of the Antoine Equation. The Antoine equation (eq 1) was used to correlate the relationship between the saturation temperature and vapor pressure for EPDMOS and EPDEOS and was solved using a weighted least-squares regression method with Eviews software (Version 5.0).¹⁶ The parameters A, B, and C of eq 1 determined with different weighted factors are listed in Tables S1a and S2a (in the Supporting Information), together with each standard errors. Their corresponding coefficient covariance matrixes were provided in Tables S1b and S2b (in the Supporting Information). Values of the standard deviations of the fit $(\sigma_{\rm F})$, as defined in eq 2, are also provided in Tables S1a and S2a. The regression results are evaluated on the basis of the lowest value of $\sigma_{\rm F}$. Values of the sum squared residuals (SSR) between the experimental saturation temperature and the fitted ones are also used as an auxiliary criterion to determine which is the most proper weighted factor because values of $\sigma_{\rm F}$ with 2 significant figures reported in Tables 1a and 2a could yield almost the same results for different weighted factors and thus the best regression is hard to be distinguished. For those regressions with the same lowest $\sigma_{\rm F}$ value and the same SSR value, values of the standard errors for parameters A, B, and C are compared and the proper weighted factor that yields the lowest standard errors for parameters could be determined. The best regression results are listed in Table 3, together with the values of the standard deviations of the fit ($\sigma_{\rm F}$). As an illustration, the regressed curves are shown in Figure 1.

$$\log p^{s} = A - \frac{B}{C + (T/K)}$$
(1)

$$\sigma_{\rm F} = \left[\sum_{i=1}^{n} \left(T_{\rm exptl,i} - T_{\rm calc,i}\right)^2 / (n-m)\right]^{1/2}$$
(2)

Table 2. Experimental and Calculated Saturation Temperatures T and Calculated Vaporization Enthalpies, $\Delta_s^{\delta} H_m^{0,a}$

p^{s}	T_{exptl}	$T_{\rm calc}$	$\Delta_l^g H_m^0$	AD ^b
kPa	К	К	kJ·mol ^{−1}	K
		EPDMOS		
2.035	373.53	373.64	56.45	0.11
3.035	382.10	382.04	55.76	0.06
4.035	388.41	388.35	55.25	0.06
5.035	393.45	393.46	54.85	0.01
6.035	397.78	397.77	54.50	0.01
7.035	401.60	401.52	54.19	0.08
9.035	407.85	407.84	53.68	0.01
11.035	413.14	413.09	53.26	0.05
13.035	417.63	417.61	52.90	0.02
16.035	423.35	423.40	52.44	0.05
19.035	428.51	428.37	52.02	0.14
22.035	432.86	432.72	51.67	0.14
25.035	436.68	436.62	51.36	0.06
28.035	439.99	440.15	51.10	0.16
31.035	442.88	443.38	50.86	0.50
37.035	449.11	449.16	50.36	0.05
40.035	451.67	451.77	50.15	0.10
43.035	454.20	454.22	49.95	0.02
46.035	456.35	456.54	49.78	0.19
49.035	458.80	458.74	49.58	0.06
52.035	460.83	460.83	49.42	0.00
55.035	462.89	462.83	49.25	0.06
58.035	465.00	464.75	49.08	0.25
61.035	466.79	466.59	48.94	0.20
		EPDEOS		
3.000	400.94	401.12	57.70	0.18
4.000	408.11	407.89	57.18	0.22
5.000	413.43	413.36	56.79	0.07
16.000	444.87	445.37	54.50	0.50
19.000	450.61	450.66	54.08	0.05
22.000	455.77	455.31	53.71	0.46
25.000	459.73	459.47	53.42	0.26
28.000	463.28	463.24	53.16	0.04
31.000	466.73	466.69	52.91	0.04
46.000	479.98	480.73	51.95	0.75
49.000	482.71	483.08	51.75	0.37
52.000	485.65	485.32	51.53	0.33
55.000	487.6	487.45	51.39	0.15
58.000	489.67	489.49	51.24	0.18
61.000	491.55	491.45	51.10	0.10
64.000	493.36	493.34	50.97	0.02

^{*a*}The standard uncertainty in temperature is u(T) = 0.02 K and the relative standard uncertainty in pressure is $u_r(p) = 2$ %. ^{*b*}Absolute deviations (AD) = $|T_{exptl} - T_{calc}|$, where T_{exptl} is the experimental value and T_{calc} is calculated from the Antoine equation.

where T_{exptl} is the experimental data, T_{calc} is the fitted data calculated using the Antoine eq (eq 1), *n* is the number of experimental points used in the fit, and *m* is the number of adjustable parameters in the Antoine equation.

Values of the saturation temperature for EPDMOS and EPDEOS at each experimental pressure were calculated from the Antoine equation with parameters A, B, and C listed in Table 3 and compared with the respective experimental values as shown in Table 2. The maximum absolute deviation between the calculated value and the experimental data was 0.50 K and

chemical name	A	В	С	$p_{\min} - p_{\max}$	$\sigma_{ m F}$
			K	kPa	K
EPDMOS	9.1280 ± 0.0633	1590.18 ± 40.49	-100.39 ± 4.04	2.035-61.035	0.16
EPDEOS	9.1049 ± 0.1744	1678.64 ± 119.53	-102.84 ± 12.11	3.0-64.0	0.34

Table 3. Regressed Parameters of Antoine Equation, Equation 1, for EPDMOS and EPDEOS



Figure 1. Vapor pressure curves: \blacktriangle , EPDMOS; \bigtriangledown , EPDEOS; solid lines, the fitted Clark–Glew equation and Antoine equation.

0.75 K for EPDMOS and EPDEOS, respectively. These high dispersions might be related to the unbalanced gas-liquid equilibrium resulted from the heat loss at higher temperatures or the possible hydrolysis, condensation, and polymerization reactions conducted between EPDMOS or EPDEOS and the accumulated moisture in the air inhaled through the pressure regulating valve of DPI \$15 precision pressure controller.

3.2. Regression of the Clarke–Glew Equation. In addition to the Antoine equation, the experimental saturated vapor pressure data could be correlated using the Clarke–Glew equation (eq 3).¹⁸ The advantage of the Clarke–Glew equation is that important thermodynamic parameters such as the standard vaporization Gibbs energy $[\Delta_i^{g}G_m^0(\theta)]$ (the difference in molar Gibbs energy between the gaseous phase, considered as an ideal gas and the liquid phase at the selected reference pressure and temperature), the standard vaporization enthalpy $[\Delta_i^{g}H_m^0(\theta)]$, and the difference between the heat capacity of the ideal gas and the liquid phase $[\Delta_i^{g}C_{p,m}^0(\theta)]$ can be determined using a regression of the Clarke–Glew equation¹⁹

$$R\ln\left(\frac{p^{s}}{p^{0}}\right) = -\frac{\Delta_{l}^{g}G_{m}^{0}(\theta)}{\theta} + \Delta_{l}^{g}H_{m}^{0}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + \Delta_{l}^{g}C_{p,m}^{0}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right]$$
(3)

where p^s is the vapor pressure, p^0 is the selected reference pressure ($p^0 = 10^5$ Pa), θ is the selected reference temperature ($\theta = 298.15$ K), and *R* is the molar gas constant (R = 8.314462J·K⁻¹·mol⁻¹).

As stated by Fulem et al.,¹⁹ use of the Clarke–Glew equation (eq 3) with three parameters is adequate for a given temperature range. Therefore, the experimental data listed in Table 2 were also fitted with the Clarke-Glew equation by a weighted least-squares regression method with different weighted factors and the results are shown in Tables S3a and S4a (in the Supporting Information), and their corresponding coefficient covariance matrixes are provided in Tables S3b and S4b (in the Supporting Information). The regression results are evaluated with the same method as introduced in former section. The regressions of the fit obtained with the Clarke-Glew equation are graphically shown in Figure 1. The proper parameters in eq 3 together with the standard deviation of the fit ($\sigma_{\rm F}$) as defined in eq 2 (with the exception that $T_{\rm calc}$ is the smoothed data calculated using the Clarke-Glew equation, eq 3) are presented in Table 4.

As shown in Figure 1, the Clarke–Glew and Antoine equations exhibit good correlations between the model and experimental data when they were used within the experimental pressure or temperature range. The curves almost overlapped, and they matched the experimental data well. However, when the Clarke–Glew and Antoine equations were compared in the fractional deviation plot (Figure 2), it was found that the maximum absolute deviations and relative differences between the experimental and smoothed data calculated using the Antoine equation.

As shown in Tables 3 and 4, the Clarke–Glew gave standard deviations ($\sigma_{\rm F}$) in evaluation of the overall dispersion of the residuals between the model and experimental data for both EPDMOS and EPDEOS with values of 0.14 K and 0.33 K, respectively, which were close to those obtained using the Antoine equation for both EPDMOS ($\sigma_{\rm F} = 0.16$ K) and EPDEOS ($\sigma_{\rm F} = 0.34$ K). Because these differences are not significant, both the Clarke–Glew equation and the Antoine equation were used to calculate the saturated pressures of ethylphenyldialkoxysilane at the reduced temperature ($T = 0.7 \cdot T_c$) for the estimation of acentric factors.

3.3. Extrapolated Normal Boiling Points. Because EPDMOS and EPDEOS belong to high boiling point chemicals, they react readily with atmospheric moisture through hydrolyzable diethoxy groups under higher temperature. Therefore, accurate measurements of the normal point for such substances are difficult to obtain. Apart from experimental measurements, the normal boiling point of a chemical can be extrapolated from the empirical equations with determined parameters.

Table 4. Parameters of Clarke–Glew Equation, Equation 3, at Reference Temperatures θ = 298.15 K and Pressure p^0 = 10⁵ Pa

chemical name	$\Delta_l^g G_m^0$	$\Delta_{l}^{g}H_{m}^{0}$	$\Delta^g_l C^0_{p,m}$	$(p_{\min} - p_{\max})$	$\sigma_{ m F}$
	J·mol ⁻¹	J·mol ^{−1}	$J \cdot K^{-1} \cdot mol^{-1}$	kPa	K
EPDMOS	21713.00 ± 44.81	62522.38 ± 276.25	-80.56 ± 2.18	2.035-61.035	0.14
EPDEOS	24556.29 ± 299.13	65188.54 ± 1625.34	-72.83 ± 10.98	3.0-64.0	0.33



Figure 2. Relative deviation of the experimental saturation temperatures T_{exptl} of (a) EPDMOS and (b) EMDEOS from 2035 Pa to 64 000 Pa from T_{calc} obtained in this work: O, Antoine equation; \blacktriangle , Clarke–Glew equation.

The extrapolated normal boiling points for EPDMOS and EPDEOS were calculated by the Antoine and Clarke–Glew equations with parameters listed in Tables 3 and 4, and the results are presented in Table 5. The Clarke–Glew and Antoine equations are not recommended for extrapolation once parameters were out of the applicable pressure or temperature range. However, when saturation temperatures higher than the applicable range are necessary in the design or as a guide for operation, both the Clarke–Glew and Antoine equations should be used with caution.

3.4. Standard Molar Enthalpy of Vaporization. When the vapor pressure data are regressed using the Clarke–Glew equation (eq 3), the standard molar enthalpies of vaporization for EPDMOS and EPDEOS at T = 298.15 K, $\Delta_1^g H_m^0(298.15$ K) are 62.52 ± 0.28 and 65.19 ± 1.63 kJ mol⁻¹, respectively.

Because the Clarke–Glew equation (eq 3) was used with three parameters, the temperature dependence of $\Delta_1^{\rm g} H_m^0(T)$ in the studied temperature interval results in a linear equation.¹⁹ The molar enthalpies of vaporization for EPDMOS and EPDEOS at each saturation temperature were calculated using eq 4 and the results are shown in Table 1

$$\Delta_l^g H_m^0(T) = \Delta_l^g H_m^0(298.15 \text{ K}) + \Delta_l^g C_{p,m}^0(298.15 \text{ K})$$
$$(T - 298.15 \text{ K})$$
(4)

where $\Delta_i^{g} C_{p,m}^0(298.15 \text{ K})$ is the difference between $C_{p,m}^{g,0}(298.15 \text{ K})$ and $C_{p,m}^{l}(298.15 \text{ K})$ as presented in eq 5

$$\Delta_l^g C_{p,m}^0(298.15 \text{ K}) = C_{p,m}^{g,0}(298.15 \text{ K}) - C_{p,m}^l(298.15 \text{ K})$$
(5)

The value of $\Delta_l^g C_{p,m}^0(298.15 \text{ K})$ for EPDMOS and EPDEOS result from the vapor pressure data are $-80.56 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $-72.83 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively.

To estimate the uncertainty of the vaporization enthalpy, experimental data were correlated with the linear equation, $\ln(p^s) = f(T^{-1})$ and fitted using the least-squares method. If uncertainties in $\Delta_i^g C_{p,m}^0$ are not taken into account, the uncertainty in the enthalpy of vaporization is assumed to be identical with an average deviation of experimental $\ln(p^s)$ from this linear correlation.²⁰

3.5. Acentric Factor ω . The acentric factor (ω , eq 9), which is also known as the eccentricity, is defined as the ratio of the distance between two focal points to the length of the major axis of an elliptical molecule. The acentric factor is a specific constant to measure the flat or nonspherical degree of the molecules and it reflects the molecular shape and substance polarity. Larger eccentricity factors imply greater molecular polarity. The acentric factor was first introduced in 1955 by Pitzer, has been proven to be a useful parameter for the description of matter, and has become a standard for the phase characterization of single and pure components. In addition to molecular weight, critical parameters such as critical temperature, pressure, and volume are also important state description parameters. However, critical parameters are still difficult to measure directly and no critical parameters for EPDMOS and EPDEOS have been reported in the literature. Therefore, critical parameters are estimated mainly by a group contribution method with known thermodynamic data.¹⁶

Nannoolal and co-workers²¹ proposed a new group contribution method to estimate critical property data for pure organic chemicals including some silicone compounds. In comparison with traditional Lydersen²² and Joback²³ methods, this new method can be used to investigate the influence of complex structures, especially the type and number of groups attached to the central Si atom, on the estimation of critical parameters and gave more accurate results for Si-containing compounds. Therefore, the critical parameters, which include

Table 5. Properties of EPDMOS and EPDEOS								
chemical name	T _b ^a	T _b ^b	T_b^c	T _c	Pc	Vc	ω^d	ω ^e
	K	K	K	K	kPa	cm ³ ·mol ^{−1}		
EPDMOS	487.35 ± 9.0	486.14	486.52	687.00	2416.88	657.11	0.4343	0.4373
EPDEOS	526.75 ± 9.0	512.35	512.59	698.34	1912.22	791.06	0.5255	0.5256

^{*a*}Literature value in ref 14 calculated using ACD/Laboratories Software V11.02. ^{*b*}Extrapolated value from Antoine equation with parameters listed in Table 3. ^{*c*}Extrapolated value from Clarke–Glew equation with parameters listed in Table 4. ^{*d*}The acentric factor calculated with the Clarke–Glew equation. ^{*c*}The acentric factor calculated with the Antoine equation.

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critical EPDMOS and EPDEOS temperature (T_c) , pressure (p_c) , and volume (V_c) were estimated using this method, as shown in eqs 6 to 8.

$$T_{\rm c} = T_{\rm b} \left(b + \frac{1}{a + (\sum_{i=1}^{N} N_i C_i + {\rm GI})^c} \right)$$
(6)

$$\frac{P_{\rm c}}{\rm kPa} = \frac{M^{b}(\rm g/mol)}{(a + \sum_{i=1}^{N} N_{i}C_{i} + {\rm GI})^{2}}$$
(7)

$$\frac{V_{\rm c}}{10^{-6} \,{\rm m}^3 \cdot {\rm mol}^{-1}} = \frac{\sum_{i=1}^N N_i C_i + {\rm GI}}{N^a} + b \tag{8}$$

where N_i is the number of groups of type *i*; C_i is the group contribution of group *i*; *M* is the molecular weight (g·mol⁻¹); *a*, *b*, and *c* are adjustable parameters listed in Table 6; *N* is the

Table 6. Parameter Values for Equations 6 to 8

property	а	b	с
$T_{\rm c}$	0.9889	0.6990	0.8607
$P_{\rm c}$	0.00939	-0.14041	
$V_{\rm c}$	-0.2266	86.1539	

number of atoms in the molecule (except hydrogen); and GI is the total group interaction contribution. Detailed procedures for estimation of the critical properties of EPDMOS and EPDEOS are shown in Tables S5a to S5f (in the Supporting Information) and the estimated parameters are listed in Table 5.

The acentric factor ω is defined as

$$\omega = -\log_{10}(p_r^{\text{sat}}) - 1$$
 at $T_r = 0.7$ (9)

where T_r is the reduced temperature $(T_r = T/T_c)$ and $p_r^{sat} = p^s/T_r$ p_c is the reduced vapor saturation pressure. When values of p^s at $T = 0.7 \cdot T_c$ are calculated using either the Antoine (eq 1) or the Clarke–Glew equation (eq 3), the acentric factors ω of EPDMOS and EPDEOS are calculated from the deduced vapor saturation pressure and the results are given in Table 5. The saturated vapor pressure of EPDEOS at $T_r = 0.7$ falls within the range of the measurements and both the Clarke-Glew equation and the Antoine equation give almost the same value of the saturated vapor pressure at $T_r = 0.7$. Therefore, these two models yield almost the same acentric factor ω for EPDEOS. Unfortunately, the saturated vapor pressure of EPDMOS at $T_r = 0.7$ is out of the range of the measurements and these two models give different values of the predicted saturation vapor pressure at $T_r = 0.7$ (88.91 kPa from eq 1 and 88.30 kPa from eq 3), which yield different values of the acentric factor ω for EPDMOS (0.4343 vs 0.4373). Just as mentioned above, both the Clarke-Glew and Antoine equations are not recommended for extrapolation once parameters were out of the applicable pressure or temperature range.

4. CONCLUSION

The saturation temperature of EPDMOS and EPDEOS at various pressures ranging from 2.035 kPa to 64.0 kPa was determined by means of an inclined ebulliometer. To our knowledge, this is the first study that reports on the saturation temperature of these two compounds. The Antoine and Clarke–Glew equations were fitted to the data using the

weighted least-squares regression method. Both equations exhibit a good correlation between the model and experimental data, and both sets of regressed parameters could satisfy the estimation requirements for the development and design of the chemical separation process. The fractional deviations of the experimental saturation temperatures of EPDMOS and EPDEOS in the experimental pressure range from values calculated from the Clarke–Glew equation are lower than those from values calculated from the Antoine equation since the Clarke–Glew equation of fit ($\sigma_{\rm F}$) than the Antoine equation.

Regression using the Antoine equation gives Antoine parameters (A = 9.1280, B = 1590.18, C = -100.39 K and A = 9.1048, B = 1678.64, C = -102.84 K) for EPDMOS and EPDEOS, respectively. When using the Clarke–Glew equation, the standard vaporization enthalpy at 298.15 K, $\Delta_{\rm f}^{\rm g} H_m^0$ (298.15 K) and the difference between the heat capacities of the ideal gas and the liquid phase at 298.15 K, $\Delta_{\rm f}^{\rm g} C_{\rm p,m}^0$ (298.15 K) were determined. The values of $\Delta_{\rm f}^{\rm g} H_m^0$ (298.15 K) for EPDMOS and EPDEOS are 62.52 ± 0.28 kJ·mol⁻¹ and 65.19 ± 1.63 kJ·mol⁻¹, respectively, and their $\Delta_{\rm f}^{\rm g} C_{\rm p,m}^0$ (298.15K) values are -80.56 ± 2.18 J·mol⁻¹·K⁻¹ and -72.83 ± 10.98 J·mol⁻¹·K⁻¹, respectively.

The critical parameters of these two compounds are estimated from the group contribution and group interaction method. When the saturated vapor pressures at the reduced temperatures are calculated using the Clarke–Glew equation, the acentric factors, ω , of EPDMOS and EPDEOS are estimated to be 0.4373 and 0.5256, respectively. When the saturated vapor pressures at the reduced temperatures are calculated using the Antoine equation, the acentric factors, ω , of EPDMOS and EPDEOS are estimated to be 0.4343 and 0.5255, respectively.

The Antoine parameters, Clarke–Glew parameters, acentric factors, and the molar enthalpies of vaporization obtained for EPDMOS and EPDEOS are useful fundamental data for industrial separation processes.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.5b00255.

Results of the weighted least-squares regression and their coefficient covariance matrixes of the Clarke–Glew equation and the Antotine equation for EPDMOS and EPDEOS are listed in Tables S1a to S4b. The estimation of the critical properties of EPDMOS and EPDEOS are presented in Tables S5a to S5f. (PDF)

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Notes

The authors declare no competing financial interest.

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