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Excess Molar Enthalpies for the Binary Systems of Benzene or Cyclohexane with 1,1-Diethoxyethane at 323.15 K or with 2,2-Dimethoxybutane at 303.15 K and Infinite Dilution Activity Coefficients in 1,1-Diethoxyethane

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Excess molar enthalpies, H^E, for the binary systems of benzene or cyclohexane with 1,1-diethoxyethane at 323.15 K and with 2,2-dimethoxybutane at 303.15 K are presented. Additionally, infinite dilution activity coefficients for benzene and cyclohexane in 1,1-diethoxyethane have been measured between 293.08 K and 323.15 K. The heat of mixing measurements have been carried out by means of a commercially available Hart Scientific (model 7501) flow calorimeter with an estimated accuracy of better than ±1% over the whole composition range. For the description of the experimental data a Redlich−Kister polynomial was used. The infinite dilution activity coefficients have been measured using the dilutor technique. The experimental results were compared with those predicted by the modified UNIFAC (Dortmund) model using the available interaction parameters for the "ether" group. The aim of this work is to supplement the available database for acetal systems required for the introduction the new "acetal" group in the modified UNIFAC (Dortmund) model.

Introduction

Acetals are oxygenated organic compounds used as starting materials for perfumes, agricultural chemicals, pharmaceuticals, and fragrances, for flavoring alcoholic drinks, and more recently, as oxygenated additives to diesel and environmental fuels, since they can drastically reduce the emission of CO or decrease the auto ignition temperature.[1] Acetal compounds belong to the main classes of oxaalkanes. Preliminary extensive studies on proximity effects in terms of group contribution models have already demonstrated this effect for oxaalkanes, including linear and cyclic acetals.[2−8] It is well-known that the group contribution method UNIFAC does not account for proximity effects (the variation of the interaction parameters of a given functional group in a molecule caused by the proximity of another, identical or different, functional group in the same molecule). Therefore, when these effects are very strong, it is a rule to account for these effects by introducing a new structural group. It seems to be the case for the "acetal" group, since preliminary investigations have shown that by using the "ether" group poor results are obtained for the acetal systems studied.[9,10] To overcome this problem, a new structural group for acetals will be introduced in the modified UNIFAC (Dortmund) model.[11,12] To obtain the best representation of the real behavior of the systems across the whole composition range and a large temperature range, the required group interaction parameters are fitted simultaneously to all available reliable experimental data (vapor−liquid equilibria (VLE), liquid−liquid equilibria (LLE), azeotropic data, solid−liquid equilibria of eutectic systems (SLE), excess enthalpies (H^E), activity coefficients at infinite dilution (γ^∞), etc.).[13,14]

The present work represents a continuation of the project concerning the phase behavior of systems containing acetal compounds. Azeotropic behavior for various binary systems containing diethoxymethane and 2,2-dimethoxybutane has been presented previously.[9,10] Very recently, new solid−liquid equilibrium data for binary systems of benzene and cyclohexane with three different acetal compounds, namely diethoxymethane, 2,2-dimethoxybutane, and 1,1-diethoxyethane, were presented. SLE data deliver the supporting information for the group contribution model in the low-temperature range from 193 K to 280 K. Heats of mixing data were already published for several binary systems with diethoxymethane at high temperature (393.15 K).[9] Although a large number of H^E measurements have been reported, a search in the Dortmund Data Bank[15] shows that the results at temperatures other than around room temperature are still scarce. For acetal systems they are not even far from sufficient. The Gibbs−Helmholtz relation together with information on excess enthalpies allows a quantitative temperature extrapolation of the excess Gibbs energy, G^E, and respectively the activity coefficients. Therefore, these types of data are very useful for fitting the reliable temperature dependent G^E model parameters or the required group interaction parameters for the modified UNIFAC (Dortmund) model. Beyond the theoretical importance in developing predictive models, activity coefficients at infinite dilution are very useful for judging the selectivity of solvents for processes, such as extractive distillation and extraction.

In the present paper, molar excess enthalpy, H^E, data are reported for the binary systems of benzene or cyclohexane with 1,1-diethoxyethane at 323.15 K and with 2,2-dimethoxybutane at 303.15 K. During the experiments, it

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was observed that the acetal compounds under study, especially 2,2-dimethoxybutane, are not stable at higher temperatures; therefore, the measurements of H^E were only carried out at moderate temperatures. Additionally, infinite dilution activity coefficients for the solutes benzene and cyclohexane in the more stable acetal (1,1-diethoxyethane) have been performed between (293.08 and 323.15) K and partial molar excess enthalpies at infinite dilution have been derived and compared with the values obtained from H^E measurements. But up to now no experimental values for γ^∞ are available for comparison.[15] The heat of mixing measurements have been carried out by means of a commercially available Hart Scientific (model 7501) flow calorimeter, and activity coefficients at infinite dilution have been determined by means of the dilutor technique. For the description of the experimental H^E data, a Redlich−Kister polynomial was used. Only for the system benzene + 1,1-diethoxyethane at 298.15 K,[16] H^E data have been found in the literature.[15] The experimental H^E and γ^∞ data are compared with those predicted by the modified UNIFAC (Dortmund) group contribution model using the available “ether” main group parameters. The aim of this work is to supplement the available database for acetal systems required for the introduction of the new “acetal” group in the modified UNIFAC (Dortmund) model.

Experimental Section

Benzene and cyclohexane were purchased from Scharlau (>99.9% purity checked by gas chromatography, GC), 1,1-diethoxyethane was provided by Aldrich (>99.7% purity checked by GC), and 2,2-dimethoxybutane was obtained from Roche. The latter was purified by distillation using a distillation column with 50 theoretical stages. The purity > 99.5% was checked by gas chromatography. Before their use the chemicals were stored over 3 Å molecular sieves.

For the excess enthalpy measurements, a commercially available isothermal flow calorimeter from Hart Scientific (model 7501) was used as described elsewhere.[17] The calorimeter consists of two solvent pumps (ISCO, LC 2600, 260 cm^3), a thermostated flow cell, and a back pressure regulator which prevents evaporation. The flow cell with a pulsed heater, a calibration heater, a Peltier cooler, and a mixing tube wound around a copper cylinder[18] is located in a stainless steel cylinder which is immersed in a thermostat. The calibrated liquid pumps were maintained at 298.15 K for all studied systems. Silicon oil is used as thermostating liquid for the flow cell; therefore, the equipment can be used over the temperature range (273 to 453) K, and the pressure can be kept constant up to 14 MPa. Depending on the H^E values and the flow rate for the different systems, the power per pulse can be varied between (0.05 and 20) μJ. The exact energy per pulse is obtained by calibration using the energy dissipated from a precise resistor fixed at the cylinder of the flow cell. The temperature of the flow cell is maintained constant by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler and the heat of mixing effect. From the recorded frequency change of the pulsed heater, the flow rate, the pure components’ densities, and the molar mass of the components, the molar excess enthalpies can be calculated using the energy evolved per pulse. The temperatures of the liquid pumps and of the thermostat are monitored with Hart Scientific platinum resistance calibrated thermometers (model 1006 Micro-Therm) with an accuracy of ±0.005 K. The uncertainty in H^E is estimated to be less than ±1%, as shown previously.[17] Studies of test mixtures indicated that the precision of the results was better than ±1% over the whole composition range.

The activity coefficients at infinite dilution for benzene and cyclohexane in 1,1-diethoxyethane were measured using the dilutor technique described in detail elsewhere.[19] The principle of the measurement is that a highly diluted component is stripped from the solvent (solvent mixture) by a constant inert gas flow. The variation of the solute concentration in the vapor phase is recorded by a gas chromatograph. Basically, the carrier gas (helium of very high quality: Messer-Griesheim, purity 99.996%) is brought to the desired temperature using a heating coil immersed in one thermostat (Lauda S, temperature constancy 0.01 K). Then, it is saturated with the solvent in a presaturation cell. Both presaturation and measurement cells, immersed in the same thermostat, are fitted with eight thin stainless steel capillaries (inner diameter 0.1 mm) through which the carrier gas is introduced. The smooth flow of the gas in the whole volume of the cells through all capillaries ensures that phase equilibrium is reached. After the saturation with the solvent in the presaturation cell, the carrier gas passes the measurement cell, which is filled with the same solvent and the highly diluted solute. Finally, at different periods of time, samples of 250 μL of carrier gas + solute + solvent are injected automatically via an electrical six-way valve (VICI, Valcon Instruments Co. Inc.) into the gas chromatograph (Hewlett Packard, model 6890) equipped with an FID detector and analyzed. The logarithm of peak area for the solute is recorded as a function of time. Because the measurements are carried out at high dilution, linear dependence is observed. It should be mentioned that the quantitative peak areas are not required for the data evaluation, but only their variation with time. The measurement cell contains a Pt-100 temperature sensor (Mesurix, model 2002A-RC), a septum for the injection of very small amounts from the solute (less than 10^{-3} in mole fraction already at the beginning), and a magnetic stirrer driven by a stirring motor to improve the mass transfer between the liquid and the gas phase. The pressure in the cell is measured via the septum using a home-built mobile pressure sensor (Druck PDCR 911). For the measurements, each cell is filled with about 80 cm^3 of solvent. The mass of the solvent in the measurement cell is determined by weighing. The constant level of the solvent in this cell is permanently controlled in order to be sure that the carrier gas is saturated in the presaturation cell and no solvent is removed from the measurement cell. During our measurements (about 24 h for one experimental point), more than 20% of the solute from the measurement cell was removed by the carrier gas using flow rates between (15 and 30) mL/min. The GC column, Porapak P, 80/100 mesh with diameter $^1/_8$ in. and length 0.66 m, assured a good separation of the studied solute−solvent mixtures. The accuracy of the γ^∞ determination is estimated as better than ±2.5%.[19]

Results and Discussion

The measured excess enthalpies for the binary systems of benzene or cyclohexane with 1,1-diethoxyethane at 323.15 K and with 2,2-dimethoxybutane at 303.15 K are listed in Table 1. The Redlich−Kister expansion[20] was used to correlate the results

$$\frac{H^E}{x_1x_2}/(\mathrm{J\cdot mol^{-1}}) = \sum_j^m A_j(2x_1 - 1)^{j-1} \qquad (1)$$

Table 1. Excess Molar Enthalpy, H^E, for the Binary Systems of Benzene or Cyclohexane with 1,1-Diethoxyethane at 323.15 K and with 2,2-Dimethoxybutane at 303.15 K

x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}	x_1	H^E / J·mol^{-1}
Benzene (1) + 1,1-Diethoxyethane (2) at T = 323.15 K and P = 1.308 MPa					
0.0778	−8.26	0.5165	−25.89	0.8278	−2.94
0.1511	−15.25	0.5672	−24.15	0.8650	0.03
0.2204	−20.20	0.6157	−22.04	0.9008	2.83
0.2860	−23.85	0.6619	−18.83	0.9351	4.84
0.3481	−25.83	0.7061	−15.26	0.9682	4.76
0.4071	−26.78	0.7484	−11.61		
0.4631	−26.78	0.7889	−7.57		
Cyclohexane (1) + 1,1-Diethoxyethane (2) at T = 323.15 K and P = 1.308 MPa					
0.0648	113.4	0.4676	537.9	0.7981	412.7
0.1277	211.6	0.5188	551.1	0.8405	355.3
0.1887	298.1	0.5685	556.2	0.8819	284.9
0.2478	369.2	0.6169	544.9	0.9222	201.2
0.3052	429.2	0.6640	528.0	0.9616	109.4
0.3609	477.3	0.7099	501.3		
0.4150	513.5	0.7546	462.5		
Benzene (1) + 2,2-Dimethoxybutane (2) at T = 303.15 K and P = 1.342 MPa					
0.0747	17.40	0.4523	62.99	0.7402	64.74
0.1456	28.29	0.5056	66.65	0.7816	60.55
0.2130	37.91	0.5565	69.13	0.8215	54.73
0.2772	45.43	0.6053	69.81	0.8599	46.81
0.3383	53.72	0.6521	69.23	0.8968	38.80
0.3966	58.99	0.6970	67.71	0.9325	27.23
Cyclohexane (1) + 2,2-Dimethoxybutane (2) at T = 303.15 K and P = 1.204 MPa					
0.0623	107.7	0.4568	523.4	0.7910	400.0
0.1229	197.1	0.5079	535.8	0.8346	343.7
0.1821	280.8	0.5578	540.1	0.8773	274.8
0.2397	353.0	0.6066	534.5	0.9190	196.0
0.2960	412.1	0.6542	516.1	0.9599	108.2
0.3509	458.8	0.7008	485.4		
0.4045	496.6	0.7464	448.8		

Table 2. Fitting Parameters, A_j, for Equation 1 and Root Mean Standard Deviations, RMSD, for H^E Data

A_1	A_2	A_3	A_4	A_5	A_6	RMSD / J·mol^{-1}
Benzene (1) + 1,1-Diethoxyethane (2)						
−103.68	54.891	21.135	-42.413	125.36	166.01	0.47
Cyclohexane (1) + 1,1-Diethoxyethane (2)						
2192.4	490.09	138.40	19.092	124.08	121.97	0.97
Benzene (1) + 2,2-Dimethoxybutane (2)						
266.49	105.39	48.952	55.359	73.879	-76.978	0.33
Cyclohexane (1) + 2,2-Dimethoxybutane (2)						
2148.0	434.03	-75.616	-41.362	313.74	176.53	1.49

by means of the following objective function:[21]

$$F = \sum_i^n \left[\left(\frac{H^E}{x_1 x_2} \right)_{\text{exp}} - \left(\frac{H^E}{x_1 x_2} \right)_{\text{calc}} \right]^2 \tag{2}$$

The fitted Redlich−Kister parameters A_j together with the root mean square deviations (RMSD) are given in Table 2. The number of the parameters used to represent the experimental data depends on the molecular complexity of the H^E behavior, the quality of the data, and the number of data points available. The reliable and extensive data justify the use of six parameters. For all systems studied, the obtained RMSDs are within the estimated experimental error of 1%. Additionally, the experimental data have been compared with the predicted results using the group contribution method Modified UNIFAC (Dortmund) with the available "ether" group parameters. The results of the comparison are shown in Figures 1−4. For the system benzene + 1,1-diethoxyethane (Figure 1) they are presented together with the experimental values found in the literature at 298.15 K.[16] As can be seen in Figure 1, the system benzene + 1,1-diethoxyethane shows almost ideal S-shaped behavior (H^Evalues between (−30 and +5) J·mol^{-1}). The new experimental together with the published data indicate that with increasing temperature the system becomes still more ideal. Despite the nice S-shape prediction for the excess enthalpy of the system benzene + 1,1-diethoxyethane, the modified UNIFAC (Dortmund) model predicts an opposite temperature effect using the "ether" group parameters. In Figure 3 it can be seen that, for the benzene + 2,2-dimethoxybutane system, the modified UNIFAC (Dortmund) model, in contrast to the experimental data, even predicts exothermal behavior. For the systems of cyclohexane with 1,1-diethoxyethane or 2,2-dimethoxybutane (Figures 2 and 4) the modified UNIFAC (Dortmund) model predicts symmetric endothermal behavior. But the values predicted for both systems are higher than the experimental data.

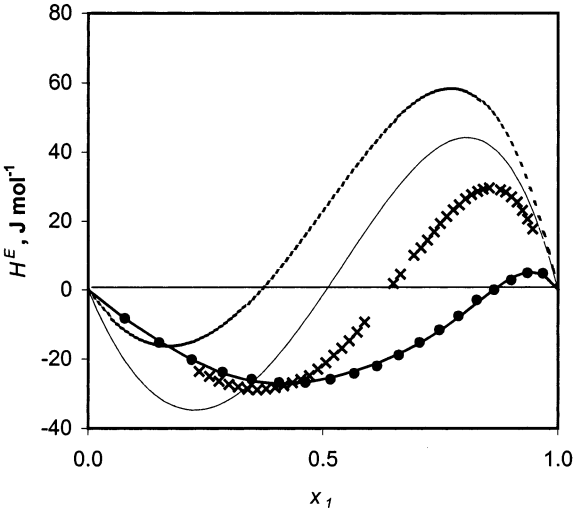

Figure 1. Experimental, correlated, and predicted H^E data for the system benzene (1) + 1,1-diethoxyethane (2): (●) our experimental data at 323.15 K and 1.308 MPa; (×) published data[16] at 298.15 K; (—) correlation of our data with the Redlich−Kister expansion; (- - -) predicted data at 323.15 K and at (- - -) 298.15 K by means of the modified UNIFAC (Dortmund) model using the "ether" group.

The experimental activity coefficients at infinite dilution for the solutes benzene and cyclohexane in the 1,1-diethoxyethane at different temperatures (293.08 K to 323.15 K) are presented in Table 3. They were obtained using the following equation:[19]

$$\gamma_i^\infty = - \frac{n_{\text{solv}} R T}{\varphi_i^s P_i^s \left(\frac{\dot{F}_{\text{He}} (1 + P_{\text{solv}}^s / P)}{a} + V_g \right)} \tag{3}$$

where n_{solv} (mol) represents the number of moles of the solvent in the measurement cell, R (J·mol^{-1}·K^{-1}) is the general gas constant, T (K) is the absolute temperature, φ_i^s is the saturation fugacity coefficient of the solute i, P_i^s (Pa) is the saturation vapor pressure of the solute i, $\dot{F}_{\text{He}}$ (m^3·s^{-1}) is the carrier gas flow, P (Pa) is the measured pressure, V_g (m^3) is the vapor space volume of the measurement cell, and a is the measured slope of the logarithm

Table 3. Infinite Dilution Activity Coefficients for Benzene and Cyclohexane in 1,1-Diethoxyethane at Different Temperatures[a]

solute		γ^∞ (at T/K)			
benzene	experimental	0.64 (293.21)	0.58 (303.16)	0.56 (313.11)	0.62 (323.13)
	modified UNIFAC	0.835 (293.15)	0.839 (303.15)	0.842 (313.15)	0.844 (323.15)
cyclohexane	experimental	1.76 (293.08)	1.72 (303.18)	1.67 (313.12)	1.64 (323.14)
	modified UNIFAC	1.402 (293.15)	1.359 (303.15)	1.314 (313.15)	1.268 (323.15)

[a] Experimental and predicted values by the modified UNIFAC (Dortmund) model using the "ether" group.

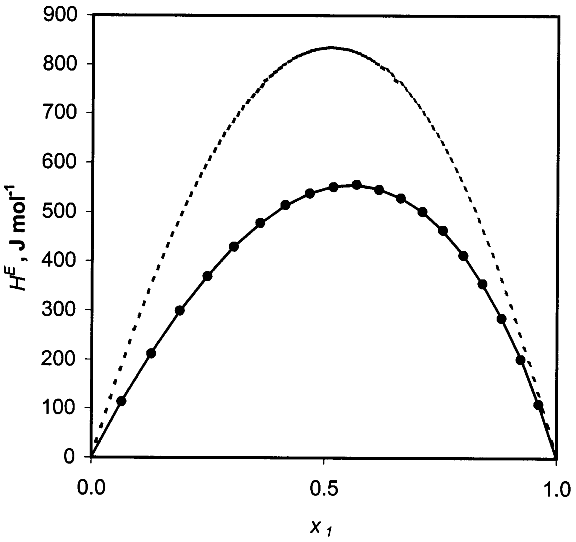

Figure 2. Experimental, correlated, and predicted H^E data for the system cyclohexane (1) + 1,1-diethoxyethane (2): (●) experimental data at 323.15 K and 1.308 MPa; (—) correlated data using the Redlich−Kister expansion; (- - -) predicted data at 323.15 by means of the modified UNIFAC (Dortmund) model using the "ether" group.

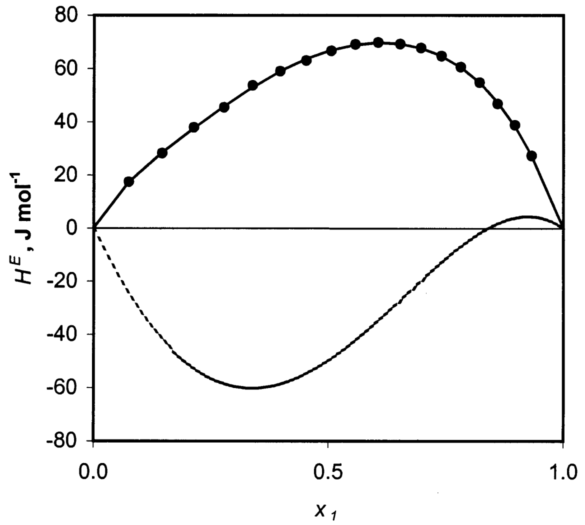

Figure 3. Experimental, correlated, and predicted H^E data for the system benzene (1) + 2,2-dimethoxybutane (2): (●) experimental data at 303.15 K and 1.342 MPa; (—) correlated data using the Redlich−Kister expansion; (- - -) predicted data at 303.15 K by means of the modified UNIFAC (Dortmund) model using the "ether" group.

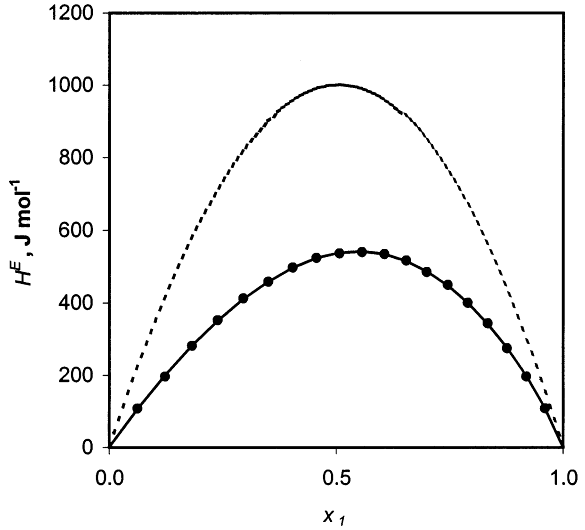

Figure 4. Experimental, correlated, and predicted H^E data for the system cyclohexane (1) + 2,2-dimethoxybutane (2): (●) experimental data at 303.15 K and 1.204 MPa; (—) correlated data using the Redlich−Kister expansion; (- - -) predicted data at 303.15 K by means of the modified UNIFAC (Dortmund) model using the "ether" group.

of the peak area for the solute i versus time. To check the correctness of the experimental activity coefficients at infinite dilution, the partial molar excess enthalpy at infinite dilution was derived from the linear dependence of the measured $\ln(\gamma_i^\infty)$ versus $1/T$ according to

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right)_{P,x} = \frac{\bar{h}_i^{E\infty}}{R} \tag{4}$$

and compared with the values obtained from the H^E measurements. A good agreement is obtained for cyclohexane (1871 J·mol^{-1} derived from γ_i^∞ compared with 1888 J·mol^{-1} derived from H^E data). The agreement is not this good for benzene (864 J·mol^{-1} derived from γ_i^∞ compared to −136 J·mol^{-1} derived from H^E data). This is understandable, since the values of γ_i^∞ for benzene are very small (as can be seen in Table 3) and the accuracy of the experimental method for the measurement of the activity coefficients at infinite dilution is about ±2.5%. In Table 3, the experimental γ_i^∞ data are compared with predicted values of the modified UNIFAC (Dortmund) model using the "ether" group. As can be seen, the predicted activity coefficients at infinite dilution are higher for benzene and smaller for cyclohexane.

Conclusion

New experimental molar excess enthalpies, H^E, for the binary systems of benzene or cyclohexane with 1,1-diethoxyethane at 323.15 K and with 2,2-dimethoxybutane at 303.15 K have been determined with an estimated accuracy of better than ±1% over the whole composition range. Additionally, new infinite dilution activity coefficients for benzene and cyclohexane in 1,1-diethoxyethane have been measured between (293.08 and 323.15) K with an accuracy of ±2.5%. For the description of the experimental H^E data, a Redlich−Kister polynomial was used. The experimental results were compared with those predicted by the modified UNIFAC (Dortmund) model using the parameters available for the "ether" main group.

Because of proximity effects, the predictions using the available “ether” group of the modified UNIFAC (Dortmund) model provide only poor results for the acetal systems investigated, as shown already previously.[9] To overcome this problem, a new structural group for acetals will be introduced in the modified UNIFAC (Dortmund) model. The aim of this paper was to supplement the experimental database for this purpose. Additional phase equilibrium measurements (VLE, γ_i^∞, etc.) for fitting temperature-dependent parameters will be carried out in the future for various acetal systems.

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