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Vapor Pressure for Mixtures of Methylene Ester Oligomers with *p*-Dioxane and Chloroform

Ruijian Xu and Jacques Léonard

CERSIM et Département de Chimie, Université Laval, Québec, Québec G1K 7P4, Canada

Van Tam Bui*

Department of Chemistry and Chemical Engineering, Royal Military College of Canada,
Kingston, Ontario K7K 5L0, Canada

Differential vapor pressures were measured for the mixtures of two linear methylene ester oligomers in *p*-dioxane and chloroform at (25, 30, 35, and 40) °C, at various concentrations. The Flory−Huggins interaction parameter χ as well as its enthalpic component κ were calculated. Large differences in interactive magnitudes between the two solvents in a given oligomer as well as between the two oligomers in a given solvent were observed.

Introduction

In a previous work (Xu et al., 1995), volume properties of cyclic oligomer solutions were compared with those of their linear counterparts and significant differences were observed between the two kinds of oligomers in a given solvent. This is mainly attributed to the large difference between the intermolecular interactions as well as to the free-volume effect, resulting from the linear and cyclic configurations of oligomers.

The interactive behavior of polymer solutions over a large range of concentration can be investigated using the Flory−Huggins lattice theory (Flory, 1953) to interpret the osmotic pressure data for very dilute solutions, the vapor pressure data for moderately concentrated solutions, or the inverse phase gas liquid chromatography data for highly concentrated solutions. Application of the Flory−Huggins theory to polymer solutions yields the interaction param- χ, which is usually concentration dependent. Nevertheless, it has been shown (Bui and Leonard, 1985, 1987) that the χ parameter could be successfully used for representing the equilibrium data of a ternary polymerization system where the polymer formed is in an equilibrium state with the remaining monomer in a given solvent. In such a system, the fluctuations of the components' compositions are relatively small such that the concentration dependency effects of the χ parameters become insignificant.

The χ parameter is related to the chemical potential of the solvent, μ_1, through (Flory, 1953)

$$\Delta\mu_1 = \mu_1 - \mu_1{}^\circ = RT[\ln(1 - \phi_2) + (1 - 1/X)\phi_2 + \chi\phi_2{}^2] \tag{1}$$

where R is the gas constant, T is the absolute temperature, X is the ratio between the partial molar volume of the oligomer, V_2, and that of the solvent, V_1, and ϕ_2 is the volume fraction of oligomer calculated by using the mole fractions x_1 and x_2 and the partial molar volumes of the two components:

$$\phi_2 = (x_2V_2)/(x_1V_1 + x_2V_2) \tag{2}$$

The chemical potential of the solvent can be readily deduced from vapor pressure data for the mixtures, and then the interaction parameter χ will be calculated through eq 1.

In the present case, since the two oligomers used are virtually nonvolatile, i.e., their vapor pressures at the working temperatures are less than the estimated experimental uncertainties, the chemical potential of the solvent is directly related to the vapor pressure of the solutions by

$$\Delta\mu_1 = RT[\ln a_1] \tag{3}$$

where a_1 is the activity of the solvent in the solution, calculated using (Booth and Devoy, 1971)

$$a_1 = (P/P^\circ) \exp[B(P - P^\circ)/RT] \tag{4}$$

where P and P° are the saturated vapor pressures of the solution and the pure solvent, respectively, and B is the second virial coefficient of the vapor phase. Experimental data for B are available for chloroform (Dymond and Smith, 1980). In the case of *p*-dioxane, B may be estimated from the Berthelot equation of state (Hirschfelder et al., 1964):

$$B = (9/128)(RT_c/P_c)(1 - 6T_c{}^2/T^2) \tag{5}$$

where P_c and T_c are the critical pressure and temperature, respectively, of *p*-dioxane (TRC, 1993).

The purpose of this work is to calculate the interaction parameter of mixtures of linear methylene ester oligomers with *p*-dioxane and with chloroform from vapor pressure measurements at four different temperatures.

Experimental Section

Materials. The oligomers used in this study are linear methylene esters of the form

$$CH_3(CH_2)_{(n/2)-1}COOCH_2OOC(CH_2)_{(n/2)-1}CH_3$$

Two different linear methylene ester oligomers, with n = 10, named LIN10 and n = 20, named LIN20, were used. Details of the synthesis procedure and the purification method are found elsewhere (Xu et al., 1995).

The solvents, *p*-dioxane and chloroform, were the highest grade available reagents. They were kept over CaH_2 and then distilled under vacuum; the middle fraction was kept over molecular sieves for further use. In order to check

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Table 1. Vapor Pressures and Calculated Values of *B* for Pure *p*-Dioxane and Chloroform

	p-dioxane			chloroform		
t/°C	$P°_{\mathrm{exp}}$/ kPa	$P°_{\mathrm{lit}}$[a]/ kPa	B[b]/ m^3·mol^{-1}	$P°_{\mathrm{exp}}$/ kPa	$P°_{\mathrm{lit}}$[a]/ kPa	B[c]/ m^3·mol^{-1}
25.0	4.973	4.986	−1.474	25.38	25.91	−1.200
30.0	6.333	6.386	−1.424	31.97	32.07	−1.150
35.0	8.067	8.129	−1.376	39.21	39.34	−1.105
40.0	10.16	10.24	−1.330	47.76	48.02	−1.065
	t_c/°C[d]				313.8	
	P_c/kPa[d]				5238.6	

[a] From Boublik, 1984. [b] Calculated using eq 5. [c] Extrapolated from Dymond and Smith, 1980. [d] From TRC, 1993.

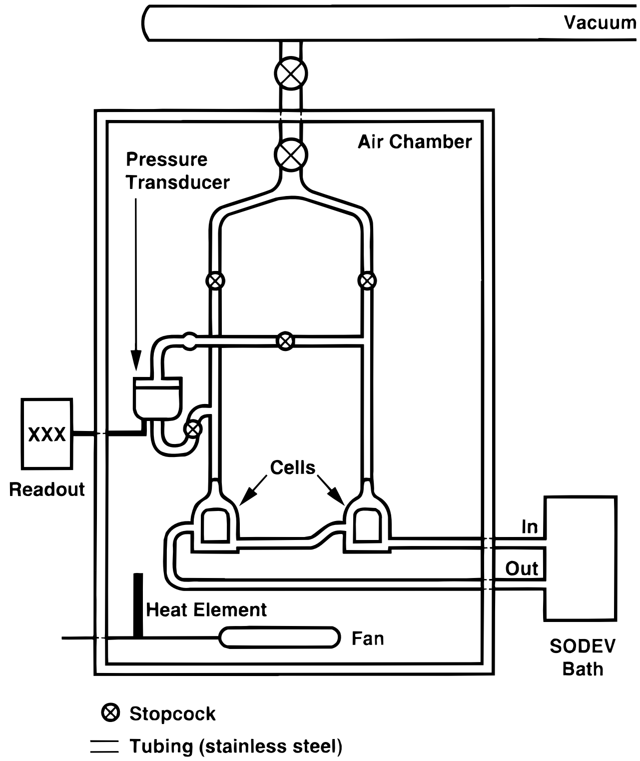

Figure 1. Apparatus for static differential vapor-pressure measurement.

the reliability of the purification method, the vapor pressures of the purified solvents at various temperatures, presented in Table 1, are compared with the data found in the literature (Boublik, 1984). There is good agreement between the two sets of values. Table 1 also lists the values P_c and T_c (TRC, 1993) for *p*-dioxane, the calculated second virial coeficient *B* for *p*-dioxane, and the extrapolated values of *B* (Dymond and Smith, 1980) for chloroform.

Vapor-Pressure Apparatus. The apparatus used for the measurement of the static differential vapor pressure of the solutions is a newly designed system illustrated by Figure 1. It is made up of a vacuum manifold, a MKS Baratron pressure transducer, type 223B, coupled with a digital readout, two identical cells containing the solvent and the solution, tubings, and stopcocks. The pressure transducer is fitted with two ports of entry where a differential pressure of up to 13.3 kPa can be measured. They are linked together through stainless steel tubings which prevent corrosion problems caused by solvent vapor and eliminate the use of *o*-rings made of elastomer materials. The volume of the double-shelled cells, including connecting tubes, is about 60 cm^3. The temperature fluctuation of solvent and mixture cells is controlled at ±0.002 deg by the circulating thermostated liquid provided by a Sodev circulating bath, model CT-B. The cells together with connecting tubings and the pressure gauge are shielded in a controlled constant temperature air chamber made of styrofoam walls and a glass window in order to prevent any vapor condensation in the tubings. With this assembly, differential pressures with a maximum fluctuation of ±1.4 Pa were measured.

Table 2. Vapor-Pressure Differences (Δ*P*/Pa) for Mixtures of Methylene Ester Oligomers with *p*-Dioxane and Chloroform at Various Concentrations and Temperatures

	t/°C			
x_2	25.0	30.0	35.0	40.0
p-Dioxane (1) + LIN10 (2)				
0.0035	17.2	22.0	28.0	35.2
0.017	84.9	108.3	138.1	174.1
0.034	167.3	213.6	272.7	344.0
0.050	247.9	316.9	404.7	510.7
0.065	326.7	417.3	533.3	674.7
Chloroform (1) + LIN10 (2)				
0.0033	83.6	103.3	126.3	153.3
0.016	420.7	519.2	634.1	768.7
0.032	850.7	1049	1279	1547
0.047	1288	1587	1933	2333
0.061	1733	2133	2600	3133
p-Dioxane (1) + LIN20 (2)				
0.0022	10.9	14.0	17.9	22.5
0.011	52.7	68.7	89.3	114.8
0.022	100.0	133.0	174.7	226.7
0.032	142.7	186.7	246.7	320.2
0.042	180.0	240.0	320.0	413.3
Chloroform (1) + LIN20 (2)				
0.0021	54.0	66.9	82.0	99.8
0.010	289.3	360.0	444.0	544.0
0.020	618.7	773.3	960.0	1181
0.030	986.7	1233	1533	1893
0.034	1387	1740	2160	2667

This maximum fluctuation was observed during the calibration of the apparatus over several hours at a fixed temperature with both cells containing the same volumes of purified chloroform.

Measurement Procedure. The whole vapor-pressure apparatus was thoroughly degassed prior to any series of measurements. The oligomer sample was precisely weighed and inserted into the mixture cell. A predetermined volume of purified solvent was then transferred to the cell by injector and degassed by operations of freezing, pumping, and melting. The freeze-and-thaw operation was repeated three times in order to make sure that no bubble formation was observed on melting. The same volume of solvent was introduced in the other cell, allowing one to measure the differential pressure between the pure solvent and the mixture. The concentrations of mixtures expressed in mole fractions are the same as used for the density measurements (Xu et al., 1995). Hence, the values deduced from density data, such as the partial molar volumes of four components could be used for further calculations.

The vapor-pressure measurements were carried out at (25, 30, 35, and 40) °C, respectively. The temperature of the mixture was allowed to reach the lowest desired value (25 °C) and then raised by increments of 5 deg to higher temperature. The vapor-pressure measurements for a set of temperatures were achieved within 1 h.

Results and Discussion

Differential vapor pressures, Δ*P* ($P = P° + \Delta P$), for the mixtures of LIN10 with *p*-dioxane and chloroform and for the mixtures of LIN20 with *p*-dioxane and chloroform at various concentrations and temperatures are listed in Table

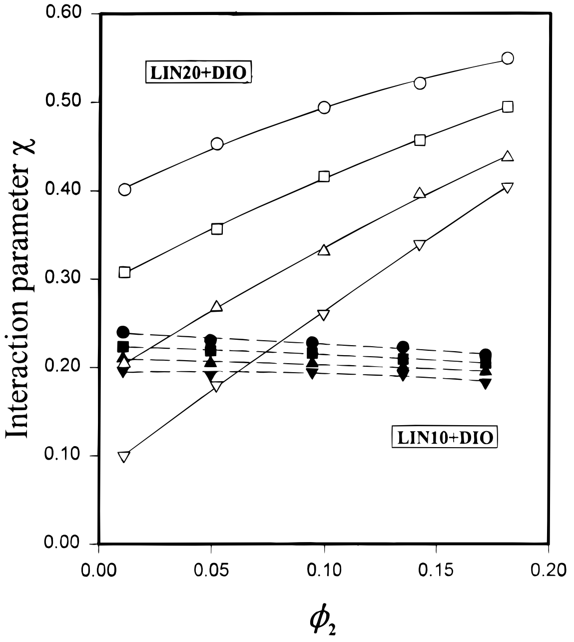

Figure 2. Interaction parameter χ for LIN10 + *p*-dioxane [●, 25 ■, 30 °C; ▲, 35 °C; ▼, 40 °C] and LIN20 + *p*-dioxane [○, 25 °C; , 30 °C; △, 35 °C; ▽, 40 °C] as a function of volume fraction ϕ_2.

Table 3. Interaction Parameters (χ) for Mixtures of Methylene Ester Oligomers with *p*-Dioxane and Chloroform at Various Concentrations and Temperatures

	t/°C			
$100\phi_2$	25.0	30.0	35.0	40.0
	p-Dioxane (1) + LIN10 (2)			
1.03	0.240	0.223	0.210	0.196
4.94	0.230	0.219	0.205	0.191
9.42	0.228	0.216	0.204	0.194
13.50	0.222	0.209	0.200	0.192
17.20	0.214	0.205	0.195	0.182
	Chloroform (1) + LIN10 (2)			
1.02	0.096	0.105	0.116	0.129
4.92	0.078	0.087	0.097	0.110
9.38	0.051	0.060	0.074	0.089
13.44	0.035	0.047	0.057	0.074
17.14	0.019	0.031	0.039	0.056
	p-Dioxane (1) + LIN20 (2)			
1.08	0.401	0.308	0.204	0.102
5.20	0.453	0.356	0.268	0.179
9.92	0.494	0.416	0.331	0.260
14.21	0.521	0.457	0.396	0.339
18.13	0.549	0.494	0.438	0.404
	Chloroform (1) + LIN20 (2)			
1.08	−0.028	−0.073	−0.120	−0.160
5.17	−0.040	−0.083	−0.123	−0.166
9.85	−0.061	−0.101	−0.134	−0.172
14.11	−0.082	−0.117	−0.143	−0.180
18.00	−0.101	−0.130	−0.160	−0.192

2. These data are used to calculate the interaction parameter, χ, using eqs 1−4. The values of χ are presented in Table 3 and plotted in Figures 2 and 3, respectively, as functions of concentration and temperature. It is noted that ϕ_2 was calculated using the available data (Xu et al., 1995) for the partial molar volumes of all oligomers and solvents studied. Due to the asymmetrical structure of chloroform as well as its three Cl atoms, this solvent shows strong interactions with both oligomers LIN10 and LIN20. These interactions are reflected by relatively small values of the χ parameter with respect to that of 0.50 for a high-molecular-weight polymer in a Θ-solvent. This type of interaction was already discussed (Xu et al., 1995) through the volumetric properties of the corresponding mixtures. Meanwhile, *p*-dioxane, with its two oxygen atoms in a cyclic symmetrical structure, shows only slight interaction with both oligomers so that the χ parameter has greater values, specially for the LIN20 oligomer. This was also supported by their volumetric properties previously reported (Xu et al., 1995). The χ parameter varied significantly with concentration for all four studied mixtures, specially the *p*-dioxane + LIN20 mixture where the interaction is weak. This variation resulted from the shortcomings of the Flory−Huggins theory based on the mean field and lattice models which do not take into account, first, the difference in sizes between the solvent molecules and the segments of polymer and, second, the long range intermolecular interactions (Bui et al., 1992) in the whole mixture. This variation is more considerable at a high temperature, 40 °C, for the *p*-dioxane + LIN20 mixture where the thermal molecular movement plays a key role in the mixing process rather than the intermolecular interaction.

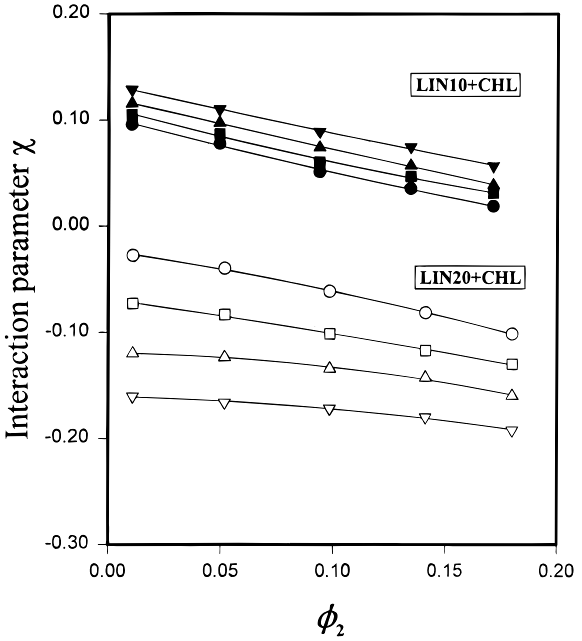

Figure 3. Interaction parameter χ for LIN10 + chloroform [●, 25 °C; ■, 30 °C; ▲, 35 °C; ▼, 40 °C] and LIN20 + chloroform [○, 25 °C; □, 30 °C; △, 35 °C; ▽, 40 °C] as a function of volume fraction ϕ_2.

From Figures 2 and 3, the parameter χ is quite sensitive to temperature, especially in the case of the LIN20 oligomer. The large number of data obtained permits the evaluation of the enthalpic parameter κ, the enthalpic component of the χ parameter, which is defined as (Flory, 1953)

$$\kappa = -T(\partial\chi/\partial T) \tag{6}$$

From the data of Table 3, expressions for χ as a function of T at a given volume fraction, using a three-term polynomial, can be obtained:

$$\chi = a + bT + cT^2 \tag{7}$$

Values of the partial derivative ($\partial\chi/\partial T$) are obtained readily from eq 7, and κ values, from eq 6. The variation of κ with the volume fraction at various T is shown in Figures 4 and 5 for the *p*-dioxane and chloroform systems, respectively. Despite the fact that the error on relatively small values of ($\partial\chi/\partial T$) may be important, κ is found to show a consistent trend for any given solute−solvent system. As expected,

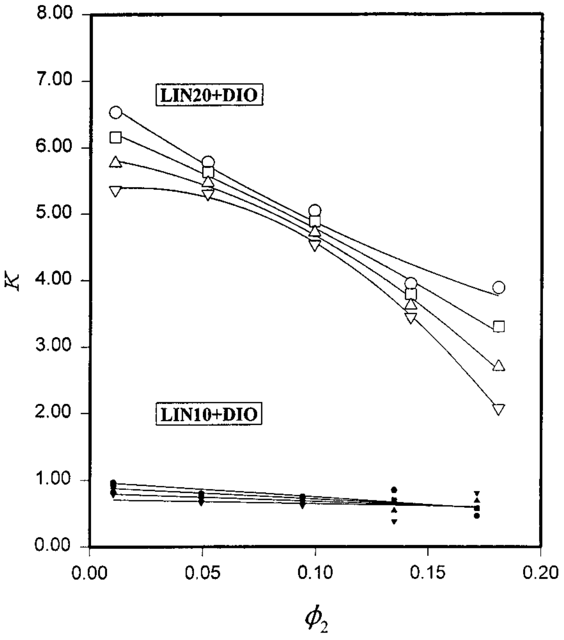

Figure 4. Enthalpic parameter κ for LIN10 + p-dioxane ●, 25 ■, 30 °C; ▲, 35 °C; ▼, 40 °C] and LIN20 + p-dioxane [○, 25 °C; , 30 °C; △, 35 °C; ▽, 40 °C] as a function of volume fraction ϕ_2.

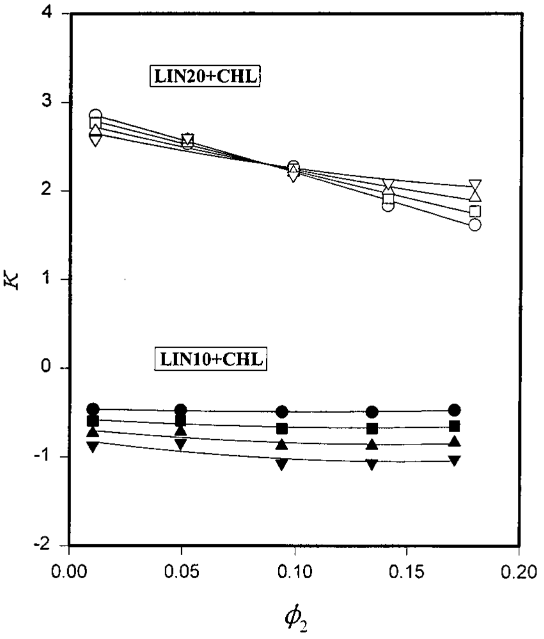

Figure 5. Enthalpic parameter κ for LIN10 + chloroform ●, 25 ■, 30 °C; ▲, 35 °C; ▼, 40 °C] and LIN20 + chloroform [○, 25 □, 30 °C; △, 35 °C; ▽, 40 °C] as a function of volume fraction

for systems where χ varies little with temperature, κ is small and almost constant with both temperature and concentration (systems with LIN10). On the other hand, larger variations of χ (systems with LIN20) lead to larger values of κ which in turn, is more concentration dependent than in the LIN10 systems. For the systems with LIN20, the result is a very large value of κ, or enthalpy of dilution, which is balanced by a very large value of the Flory Ψ, i.e. entropy of dilution, leading to a small value of the free energy parameter χ. This sort of enthalpy–entropy compensation is unusual and would be significant, probably indicating ordering of linear methylene ester oligomers having a large number of methylene groups.

The large variations of χ and κ with the oligomer in a given solvent are remarkable. This arises from the fact that the oligomers, LIN10 and LIN20, differ in "chemical nature" as well as molecular size; i.e., LIN20 is more methylene in character than LIN10. This must be why κ for chloroform + LIN10 is negative (consistent with the negative heat of mixing for ester–chloroform mixtures) but changes to positive for LIN20.

Conclusions

With a newly designed vapor-pressure apparatus, using a differential method, the vapor-pressure data for mixtures of linear methylene ester oligomers with p-dioxane and chloroform were obtained with a high accuracy at various concentrations and at four different temperatures. The Flory–Huggins interaction parameter, χ, has been calculated and shows a strong interactive pattern in the mixtures with chloroform, while only a slight interaction was observed in the mixtures with p-dioxane.

The enthalpic parameter κ was calculated from the χ data and its dependency on temperature and concentration examined.

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