(10) Spitzer, J. J.; Singh, P.; Olofsson, I.; Hepler, L. *J. Solution Chem.* **1978**, *7*, 623.
(11) Kawaizumi, F.; Nomura, H.; Nakao, F. *J. Solution Chem.* **1987**, *16*, 133.
(12) Spitzer, J. J.; Singh, P.; McCurdy, K.; Hepler, L. *J. Solution Chem.* **1978**, *7*, 81.
(13) Herrington, T.; Roffey, M.; Smith, D. *J. Chem. Eng. Data* **1986**, *31*, 221.
(14) Smith, R. M.; Martell, A. E. *Critical Stability Constants. Volume 4. Inorganic Complexes*; Plenum: New York, 1976.

Received for review October 8, 1987. Accepted February 24, 1988. This work was supported by the Department of Energy under grant De-FG01-87FE61146.

Vapor–Liquid Equilibria at 760 mmHg in the Ternary System Methanol–Propyl Bromide–Methyl Methacrylate

Jaime Wisniak* and Abraham Tamir

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel 84105

Vapor–liquid equilibrium at atmospheric pressure has been determined for the title ternary system. The data were correlated by various equations and the appropriate parameters are reported.

The present work was undertaken to measure VLE data for the ternary system methanol–propyl bromide–methyl methacrylate for which no isobaric data are available. Data for the binary systems methanol–propyl bromide and propyl bromide–methyl methacrylate have been reported elsewhere (*1*, *2*) and thermodynamically consistent isobaric data for the system methanol–methyl methacrylate have been reported by Pavlov et al. (*3*). This work is part of a program to determine the UNIFAC parameters for organic bromides.

Experimental Section

Purity of Materials. Analytical grade methanol (99.5%+) was purchased from Frutarom, propyl bromide (99.4%) from Merck, and methyl methacrylate analytical grade (99.4%+) from Fluka. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*4*) was used in the equilibrium determination. The experimental features have been described in previous publications (*5*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 200 cm long and 0.2 cm in diameter, was packed with 20% OV-17, and was operated isothermally at 100 °C. Injector and detector temperatures were 220 and 230 °C, respectively. Very good separation was achieved under these conditions, and calibration analyses were carried to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 2$ mmHg and $\Delta t = \pm 0.02$ °C.

Results

The temperature–concentration measurements at 760 mmHg for the ternary system are reported in Table II together with the activity coefficients which were calculated from the following equation (*6*)

$$\ln \gamma_i = \ln(Py_i/P_i^0x_i) + (B_{ii} - V_i^L)(P - P_i^0)/RT + (P/2RT)\sum \sum y_jy_k(2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

Table I. Physical Constants of Pure Components

index	compd	refractive index	bp(760 mmHg), °C	purity (GLC(min)), %
1	methanol	1.3280[a] (20 °C) 1.32840[b]	64.68[a] 64.70[b]	99.5
2	propyl bromide	1.4348[a] (20 °C) 1.4343[b]	70.55[a] 71.0[b] 70.80[c]	99.6
3	methyl methacrylate	1.4118[a] (25 °C) 1.4120[b]	100.4[a] 100.3[b]	99.4

[a] Measured. [b] Reference *13*. [c] Reference *14*.

Vapor pressures P_i^0 were calculated according to Antoine's equation

$$\log P_i^0 = \alpha_i - \beta_i/(\delta_i + t) \quad (3)$$

where the constants are reported in Table III. The molar virial coefficients B_{ii} and the molar mixed coefficient B_{ij} were calculated by the method of Tsonopoulos (*7*) using the molecular parameters suggested by the same author.

The ternary data reported in Table II were found to be thermodynamically consistent as tested by the McDermot–Ellis two-point method (*8*) modified by Wisniak and Tamir (*9*). Two experimental points a and b, at almost the same temperature, are considered thermodynamically consistent if the following condition is fulfilled:

$$D_{ab} < D_{max} \quad (4)$$

The local deviation D_{ab} is given by

$$D_{ab} = \sum_{i=1}^{N}(x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \quad (5)$$

where N is the number of components and the maximum local deviation D_{max} is

$$D_{max} = \sum_{i=1}^{N}(x_{ia} + x_{ib})(1/x_{ia} + 1/y_{ia} + 1/x_{ib} + 1/y_{ib})\Delta x + 2\sum_{i=1}^{N}|\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{N}(x_{ia} + x_{ib})\Delta P/P + \sum_{i=1}^{N}(x_{ia} + x_{ib})\beta_i\{(t_a + \delta_i)^{-2} + (t_b + \delta_i)^{-2}\}\Delta t \quad (6)$$

The errors in the measurements Δx, ΔP, and Δt were as previously indicated. The first term in eq 6 was the dominant one.

The activity coefficients were correlated by the following Redlich–Kister expansion (*10*)

$$\ln \gamma_1 = x_2x_3[(E_{12} + E_{13} - E_{23}) + F_{12}(2x_1 - x_2) + F_{13}(2x_1 - x_3) + 2F_{23}(x_3 - x_2) + G_{12}(x_1 - x_2)(3x_1 - x_2) + G_{13}(x_1 - x_3)(3x_1 - x_2) - 3G_{23}(x_3 - x_2)^2 + F_1(1 - 2x_1)] + x_2^2[E_{12} + F_{12}(3x_1 - x_2) + G_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2[E_{13} + F_{13}(3x_1 - x_3) + G_{13}(x_1 - x_3)(5x_1 - x_3)] \quad (7)$$

0021-9568/88/1733-0376$01.50/0 © 1988 American Chemical Society

Table II. Experimental Vapor-Liquid Equilibrium Data for Methanol (1)-Propyl Bromide (2)-Methyl Methacrylate (3) at 760 mmHg

temp, °C	x_1	x_2	x_3	y_1	y_2	y_3	γ_1	γ_2	γ_3
55.70	0.431	0.507	0.062	0.493	0.493	0.014	1.7008	1.6050	1.0731
56.01	0.611	0.333	0.056	0.514	0.468	0.018	1.2321	2.2990	1.5111
56.13	0.266	0.670	0.064	0.451	0.535	0.014	2.4814	1.2955	1.0199
56.64	0.205	0.735	0.060	0.428	0.558	0.014	2.9932	1.2090	1.0653
56.70	0.355	0.555	0.090	0.461	0.511	0.028	1.8521	1.4664	1.4196
56.70	0.252	0.670	0.078	0.430	0.548	0.022	2.4394	1.3001	1.2849
56.90	0.403	0.493	0.104	0.477	0.491	0.032	1.6715	1.5722	1.3944
57.00	0.776	0.192	0.032	0.575	0.412	0.013	1.0355	3.4101	1.8446
57.17	0.332	0.567	0.101	0.461	0.511	0.028	1.9402	1.4129	1.2421
57.20	0.452	0.429	0.119	0.502	0.456	0.042	1.5453	1.6693	1.5833
57.95	0.550	0.325	0.125	0.516	0.443	0.041	1.2625	2.0896	1.4305
58.02	0.517	0.328	0.155	0.537	0.417	0.046	1.3917	1.9473	1.2925
58.38	0.440	0.391	0.169	0.514	0.440	0.046	1.5433	1.7004	1.1675
58.45	0.636	0.239	0.125	0.567	0.387	0.046	1.1706	2.4502	1.5793
58.87	0.692	0.190	0.118	0.619	0.335	0.046	1.1504	2.6415	1.6520
59.07	0.244	0.544	0.212	0.472	0.472	0.056	2.4876	1.2781	1.1010
59.24	0.186	0.670	0.144	0.411	0.554	0.035	2.8335	1.2069	1.0034
59.56	0.118	0.769	0.113	0.387	0.587	0.026	4.1559	1.1011	0.9374
59.72	0.646	0.191	0.163	0.619	0.315	0.066	1.1884	2.4023	1.6611
59.80	0.585	0.222	0.193	0.606	0.324	0.070	1.2812	2.1182	1.4821
59.95	0.821	0.104	0.075	0.702	0.260	0.038	1.0467	3.6385	2.0725
60.00	0.400	0.350	0.250	0.521	0.409	0.070	1.6047	1.6747	1.1295
60.14	0.281	0.453	0.266	0.490	0.438	0.072	2.1397	1.3766	1.0843
60.28	0.743	0.119	0.138	0.678	0.257	0.065	1.1025	3.1031	1.8994
60.35	0.420	0.315	0.265	0.537	0.388	0.075	1.5506	1.7470	1.1277
60.61	0.833	0.081	0.086	0.724	0.224	0.052	1.0339	3.9458	2.4162
60.65	0.458	0.271	0.271	0.595	0.100	0.305	1.5493	0.5209	4.4578
60.87	0.700	0.138	0.162	0.648	0.277	0.075	1.0923	2.8217	1.8216
61.14	0.869	0.053	0.078	0.751	0.197	0.052	1.0045	5.2243	2.6164
61.19	0.463	0.246	0.291	0.569	0.336	0.095	1.4359	1.8890	1.2626
61.20	0.101	0.778	0.121	0.338	0.629	0.033	3.9695	1.1033	1.0426
61.67	0.879	0.044	0.077	0.794	0.153	0.053	1.0258	4.8221	2.6571
61.78	0.912	0.049	0.039	0.780	0.192	0.028	0.9672	5.4061	2.7559
62.14	0.468	0.202	0.330	0.597	0.299	0.104	1.4304	1.9889	1.1782
62.34	0.152	0.616	0.232	0.400	0.530	0.070	2.9607	1.1351	1.1080
62.34	0.451	0.206	0.343	0.595	0.286	0.119	1.4671	1.8533	1.2873
62.65	0.708	0.067	0.225	0.730	0.156	0.114	1.1261	3.1099	1.8758
62.84	0.712	0.063	0.225	0.731	0.151	0.118	1.1125	3.1819	1.9280
62.88	0.630	0.087	0.283	0.697	0.175	0.128	1.1981	2.6594	1.6562
62.89	0.527	0.132	0.341	0.652	0.219	0.129	1.3414	2.1850	1.3803
63.12	0.226	0.403	0.371	0.476	0.425	0.099	2.2822	1.3624	0.9553
63.18	0.360	0.235	0.405	0.565	0.311	0.124	1.6879	1.7159	1.0989
63.34	0.936	0.025	0.039	0.874	0.092	0.034	0.9882	4.8686	3.1811
63.40	0.729	0.043	0.228	0.761	0.115	0.124	1.1044	3.4957	1.9625
63.49	0.708	0.048	0.244	0.770	0.105	0.125	1.1460	2.8532	1.8437
63.67	0.266	0.335	0.399	0.500	0.381	0.119	1.9880	1.4458	1.0475
63.77	0.321	0.270	0.409	0.536	0.335	0.129	1.7552	1.5757	1.1058
63.86	0.410	0.176	0.414	0.603	0.263	0.134	1.5353	1.9007	1.1354
63.88	0.722	0.038	0.240	0.768	0.095	0.137	1.1031	3.2196	2.0245
64.43	0.567	0.047	0.386	0.715	0.095	0.190	1.2804	2.5466	1.7041
64.74	0.404	0.192	0.404	0.606	0.245	0.149	1.5101	1.5785	1.2526
65.10	0.785	0.010	0.205	0.832	0.019	0.149	1.0444	2.3663	2.4764
65.12	0.128	0.561	0.311	0.377	0.528	0.095	2.9575	1.1356	1.0117
65.25	0.516	0.057	0.427	0.707	0.111	0.182	1.3460	2.3883	1.4305
65.30	0.443	0.100	0.457	0.657	0.176	0.167	1.4564	2.1467	1.2199
65.85	0.477	0.037	0.486	0.695	0.075	0.230	1.3973	2.4372	1.5529
65.85	0.452	0.051	0.497	0.679	0.094	0.227	1.441	2.2134	1.4970
67.05	0.300	0.140	0.560	0.594	0.203	0.203	1.8162	1.6667	1.1310
67.20	0.313	0.130	0.557	0.594	0.203	0.203	1.7303	1.7866	1.1309
67.60	0.363	0.077	0.560	0.644	0.144	0.212	1.5888	2.1201	1.1613
67.63	0.401	0.033	0.566	0.691	0.068	0.241	1.5389	2.3420	1.3089
68.00	0.227	0.165	0.608	0.535	0.235	0.230	2.0865	1.5840	1.1370
69.61	0.199	0.178	0.623	0.527	0.251	0.222	2.2005	1.4918	1.0106
71.21	0.209	0.102	0.689	0.589	0.168	0.243	2.1939	1.6655	0.9481
71.35	0.258	0.023	0.719	0.604	0.041	0.355	1.8110	1.7972	1.3227
72.83	0.189	0.087	0.724	0.541	0.145	0.314	2.0967	1.6013	1.0995
73.60	0.124	0.184	0.692	0.453	0.271	0.276	2.6086	1.3772	0.9807
73.67	0.204	0.019	0.777	0.560	0.032	0.408	1.9451	1.5801	1.2946
75.28	0.136	0.071	0.793	0.486	0.119	0.395	2.3890	1.4941	1.1581
76.53	0.158	0.019	0.823	0.502	0.027	0.471	2.0250	1.2225	1.2763
86.85	0.032	0.130	0.838	0.211	0.237	0.552	2.9339	1.1664	1.0411
95.35	0.010	0.031	0.959	0.128	0.072	0.800	4.5783	1.2522	1.0784

where E_{ij}, F_{ij}, and G_{ij} are the binary constants and F_1 is a ternary constant. The equations for two other activity coefficients were obtained by cyclic rotation of the indexes. The binary data used for calculating the binary constants were reported elsewhere (*1*, *2*).

The binary and ternary Redlich-Kister coefficients were ob-

Table III. Vapor Pressure Constants

compound	α_i	β_i	δ_i
methanol (*13*)	7.897 50	1474.08	229.13
propyl bromide (*13*)	6.910 65	1194.889	225.51
methyl methacrylate (*2*)	7.109 00	1387.86	226.153

Table IV. Redlich-Kister Correlation of Binary and Ternary Data

system	B_{ij}	C_{ij}	D_{ij}	rmsd γ_1	rmsd γ_2
methanol (1)–propyl bromide (2)	1.8365	−0.3388	0.1870	0.140	0.394
methanol (1)–methyl methacrylate (3)	1.1447	−0.0407	0.4550	0.145	0.056
propyl bromide (2)–methyl methacrylate (3)	−0.5193	−0.5031	−0.03158	0.389	0.283

		overall rmsd γ	overall rmsd y
methanol (1)–propyl bromide (2)	$F_1 = 0$	1.142	0.064
methyl methacrylate (3)	$F_1 = 0.13388$	1.141	0.064

Table V. Correlation of Boiling Points, Eq 8 and 9

system	C_0	C_1	C_2	C_3	rmsd	diff,[a] %
methanol (1)–propyl bromide (2)	−49.640	6.9945	−88.093	45.579	0.97	1.2
methanol (1)–methyl methacrylate (3)	−55.530	33.9173	−81.237	96.411	1.23	1.2
propyl bromide (2)–methyl methacrylate (3)	10.635	6.9135	5.5643	0.00	0.11	0.1

system	A	B	C	rmsd	diff, %
methanol (1)–propyl bromide (2) methyl methacrylate (3)	−189.37	195.32	230.35	0.91	0.94

[a] Diff, % = $(100/n)\sum_{i=1}^{n}(|T_{\mathrm{exptl}} - T_{\mathrm{calcd}}|/T_{\mathrm{exptl}})$.

tained by a Simplex optimization technique and are reported in Table IV. The relative values of the root mean square deviation and the ternary constant F_1 suggest that ternary data can be predicted directly from the binary systems. Boiling points of the binary and ternary systems were correlated by the equation suggested by Wisniak and Tamir (*11*):

$$T = \sum_{i=1}^{2} x_i T_i^0 + x_1 x_a \left[\sum_{k=0}^{i} C_k (x_i - x_j)^k + \ldots \right] \tag{8}$$

$$T = \sum_{i=1}^{3} x_i T_i^0 + \sum_{i,j=1} \{x_i x_j \sum_{k=0}^{i} C_k (x_i - x_j)^k\} + x_1 x_2 x_3 \{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + \ldots\} \tag{9}$$

T_i^0 is the boiling point of the pure component in K and i is the number of terms in the series expansion of $(x_i - x_j)$. C_k are the binary constants where A, B, C, D are ternary constants. The various constants are reported in Table V, which also contains information indicating the degree of goodness of the correlation.

The boiling temperature of the mixture was correlated solely with the liquid composition by the following equation which has been derived on the basis of the concept of "excess property" (*12*):

$$T = \sum_{i=1}^{N} x_i T_i^0 + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} x_i x_j [A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + \ldots] \tag{10}$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures as explained in ref *12*. The coefficients A_{ij}, B_{ij}, C_{ij} are multicomponent parameters which are determined directly from the multicomponent data. Figure 1 reports the isothermals at 760 mmHg obtained on the basis of the parameters A_{ij}, B_{ij} reported in Table VI by applying eq 10 for $N = 3$. These isothermals might be used for considering possible distillation paths in ternary systems as well as to conclude whether a ternary system exhibits azeotropic behavior.

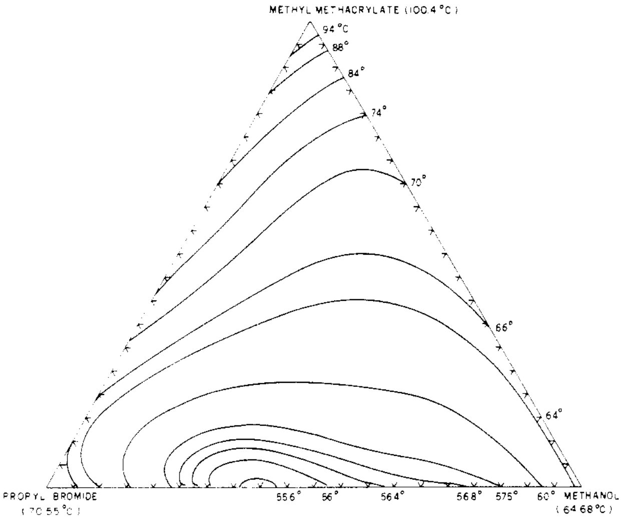

Figure 1. Isothermals for the ternary system at 760 mmHg.

Table VI. Parameters of *T*–*x* Correlation (Eq 10, *N* = 3) for Methanol (1)–Propyl Bromide (2)–Methyl Methacrylate (3) at 760 mmHg[a]

ij	A_{ij}	B_{ij}	C_{ij}	D_{ij}	mean *D*,[b] %	rmsd
12	−52.64	16.78				
13	−66.71	55.05			2.47	0.247
23	−42.66	4.711				
12	−47.07	21.47	−43.27	−30.49		
13	−58.13	44.34	−63.52	54.75	1.10	0.139
23	−37.67	5.826	−64.97	−35.53		

[a] t_1^0 = 64.68 °C; t_2^0 = 70.55 °C; t_3^0 = 100.4 °C. [b] $D = |(T_{\mathrm{exptl}} - T_{\mathrm{calcd}})/T_{\mathrm{exptl}}|$; mean D, % = $(100/n)\sum D_i$.

As observed, although the binary system methanol–propyl bromide has an azeotrope, the ternary system does not exhibit a clear azeotropic behavior. It is possible that there is a ternary azeotrope very close in composition to that of the binary azeotrope between methanol and propyl bromide. Table VI contains also the group of parameters A_{ij}, B_{ij}, C_{ij} for the T–x correlation (eq 10) which yields the smaller mean deviation between the calculated and observed values of T.

Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental and numerical determinations.

Glossary

A_{ij}, B_{ij}, ...	multicomponent adjustable parameters in eq 8
B_{ii}, B_{ij}	virial coefficients, eq 2
E_{ij}, F_{ij}, G_{ij}	Redlich-Kister constants, eq 7
n	number of experimental points
N	number of components
P	total pressure, mmHg
P_i^0	vapor pressure of pure component i, mmHg
R	gas constant, 82.06 (cm^3 atm)/(g mol K)
T	boiling temperature of a mixture, K

J. Chem. Eng. Data **1988**, *33*, 379–381

T_i^0	boiling temperature of pure component *i*, K
t	temperature, °C
x_i, y_i	mole fraction of component *i* in the liquid and vapor phases
α_i	coefficient, Antoine equation
β_i	coefficient, Antoine equation
γ_i	activity coefficient of component i
δ_i	coefficient, Antoine equation

Registry No. Methanol, 67-56-1; propyl bromide, 106-94-5; methyl methacrylate, 80-62-6.

Literature Cited

(1) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1987**, *30*, 339.
(2) Tamir, A.; Wisniak, J. submitted for publication in *J. Chem. Eng. Data*.
(3) Pavlov, S. V.; Kirnos, A. B.; Pavlova, S. P.; Lazaryants, V. E. *Zn. Prikl. Khim*. **1979**, *45*, 614.
(4) Boublikova, L.; Lu, B. C. Y. *J. Appl. Chem*. **1969**, *19*, 89.
(5) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1975**, *20*, 168.
(6) Van Ness, H. C.; Abbott, M. M. *Classical Thermodynamics of Nonelectrolyte Solutions*; McGraw-Hill: New York, 1982.
(7) Tsonoupoulos, C. *AIChE J*. **1974**, *33*, 263.
(8) McDermott, C.; Ellis, S. R. M. *Chem. Eng. Sci*. **1965**, *20*, 293.
(9) Wisniak, J.; Tamir, A. *J. Chem. Eng. Data* **1977**, *22*, 253.
(10) Redlich, O.; Kister, A. T. *Ind. Eng. Chem*. **1948**, *40*, 345.
(11) Wisniak, J.; Tamir, A. *Chem. Eng. Sci*. **1975**, *30*, 335.
(12) Tamir, A. *Chem. Eng. Sci*. **1981**, *36*, 1453.
(13) *TRC Thermodynamic Tables—Non Hydrocarbons*; Thermodynamics Research Center, The Texas A&M University System: College Station, TX, 1974.
(14) Perry, R. H. *Perry's Chemical Engineers' Handbook*, 6th ed.; McGraw-Hill: New York, 1984; p 3–58.

Received for review October 20, 1987. Accepted March 16, 1988.

Excess Enthalpies for Binary Mixtures of 2,5,8-Trioxanonane or 2,5,8,11,14-Pentaoxapentadecane with *n*-Alkanes at 298.15 K

Teresa Treszczanowicz,*[†] George C. Benson, and Benjamin C.-Y. Lu

Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 9B4

Excess enthalpies, measured at 298.15 K in a flow microcalorimeter, are reported for the binary systems formed by mixing 2,5,8-trioxanonane with *n*-hexane, *n*-decane, and *n*-dodecane, and by mixing 2,5,8,11,14-pentaoxapentadecane with *n*-hexane, *n*-heptane, and *n*-decane. All of the excess enthalpies are strongly positive, with maxima which are located near the equimolar concentration.

Introduction

Previously we reported thermodynamic properties of oligo(oxyethylene) alkyl ether–*n*-alkane mixtures containing 2,5-dioxahexane (*1*, *2*), 3,6-dioxaoctane (*3*–*5*), 2,5,8-trioxanonane (*1*, *6*, *7*), and 2,5,8,11-tetraoxadecane (*8*, *9*). Systems of this type have also been studied by Kehiaian et al. (*10*), and more recently by Booth and co-workers (*11*, *12*).

The present paper extends our previous investigations by describing measurements of the excess enthalpies for binary mixtures of 2,5,8-trioxanonane (diethylene glycol dimethyl ether) with *n*-hexane, *n*-decane, and *n*-dodecane, and of 2,5,8,11,14-pentaoxapentadecane (tetraethylene glycol dimethyl ether) with *n*-hexane, *n*-heptane, and *n*-decane. Data for such series of mixtures are needed in the development of lattice and equation of state theories for this class of systems.

Experimental Section

In the course of the present work, the 2,5,8-trioxanonane (Aldrich Chemical Co., labeled 99 mol %) was purified by fractional distillation from sodium. The 2,5,8,11,14-pentaoxapentadecane (purum, >98 mol %) was obtained from Fluka. Prior to their use, both ethers were stored over molecular sieve beads, Type 3A. The *n*-alkanes were obtained from the Phillips Petroleum Co. and were stored over Type 4A molecular sieve beads. The *n*-hexane was Research Grade (purity exceeding 99.9 mol %); the *n*-heptane, *n*-decane, and *n*-dodecane were Pure Grade (purity exceeding 99 mol %). Densities, ρ, characterizing the component liquids at 298.15 K are compared in Table I with data from the literature (*11*, *13*–*16*).

Table I. Densities, ρ, for the Component Liquids at 298.15 K

	ρ, kg m^{-3}	
component	obsd	lit.
2,5,8-trioxanonane	939.52	944.0,[a] 938.4,[b] 942[c]
2,5,8,11,14-pentaoxapentadecane	1006.51	1004.7,[d] 1007[c]
n-hexane	654.99	654.84[e]
n-heptane	679.71	679.46[e]
n-decane	726.25	726.35[e]
n-dodecane	745.35	745.18[e]

[a] Reference *13*. [b] Reference *14*. [c] Estimated from density (measured within ±2 kg m^{-3}) at 304.15 K in ref *11*, using thermal expansivity. [d] Reference *15*. [e] Reference *16*.

Molar excess enthalpies, H^E_m, were determined in a LKB flow microcalorimeter (Model 10700-1) thermostated to ±0.002 K at 298.15 K. Details of this equipment and its operation have been described previously (*17*, *18*). Over most of the mole fraction range, the errors in H^E_m and in the mole fraction x are estimated to be less than 0.5% and 5×10^{-4}, respectively.

Results and Discussion

The experimental values of H^E_m are listed in Table II, where in all cases x is the mole fraction of the polyether. The results for 2,5,8-trioxanonane are plotted in Figure 1; those for 2,5,8,11,14-pentaoxapentadecane are shown in Figure 2. The equation

$$H^E_m/\text{J mol}^{-1} = x(1 - x)\sum_{j=1}^{k} h_j(1 - 2x)^{j-1} \qquad (1)$$

was fitted to each set of results by the method of least squares with all points weighted equally. Values of the coefficients, h_j, and the standard deviations, s, for these representations are given in Table III. Curves calculated from eq 1 are shown

---

[†] Visiting Scientist from the Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland.

0021-9568/88/1733-0379$01.50/0