Excess Molar Enthalpies and Excess Molar Volumes of Diethyl Carbonate + Some *n*-Alkoxyethanols at (298.15 and 313.15) K

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Excess molar enthalpies H_m^E and excess molar volumes V_m^E of diethyl carbonate + some alkoxyethanol mixtures have been determined by an LKB flow microcalorimeter and an Anton Paar density meter as a function of mole fraction of diethyl carbonate at (298.15 and 313.15) K. The alkoxyethanols are 2-methoxyethanol, 2-ethoxyethanol, 2-buthoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, and 2-(2-butoxyethoxy)ethanol, respectively.

Introduction

Knowledge of the thermodynamic properties of organic liquid mixtures is very important in understanding the molecular interactions between the components for theoretical models and also industrial applications.

Continuing our research program involving a systematic study of the thermodynamic excess properties of binary mixtures containing diethyl carbonate + some series of organic compounds (Francesconi et al., 1997; Francesconi and Comelli, 1997; Comelli et al., 1999), in the present paper we report the excess molar enthalpies H_m^E and the excess molar volumes V_m^E for the binary mixtures formed by diethyl carbonate and *n*-alkoxy- and (*n*-alkoxyethoxy)-ethanols at atmospheric pressure and at (298.15 and 313.15) K over the entire composition range.

The alkoxyethanols considered in this paper are namely 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, and 2-(2-butoxyethoxy)ethanol.

Dialkyl carbonates are used as solvents for a variety of extractions of industrial importance, in the synthesis of pharmaceuticals, and in agricultural chemistry (Annesini et al., 1984; *Merck Index*, 1989; Martindale, 1989).

On the other hand, the thermodynamic study of mixtures containing the oxy (-O-) and hydroxy (-OH) functional groups has been of great interest (Douhèret and Pal, 1988; Pal and Sing, 1996) if the information required to characterize the molecular interactions of these groups is available.

No literature results have been found for these mixtures.

Experimental Section

Chemicals. Chemicals were Aldrich and Fluka products. Diethyl carbonate has been purified as described previously (Francesconi and Comelli, 1997) while alkoxy- and (alkoxy-ethoxy)ethanols were used as received, owing to their high-purity grade, from the purchaser.

Before measurements, pure liquids were degassed by ultrasound (ultrasonic bath, Hellma, type 460, Milan, Italy), kept in dark bottles, and dried over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets) to reduce the water content.

The analyses of the products were performed on a Hewlett-Packard gas chromatograph model 5890 using an HP (cross-linked 5% Me siloxane) capillary column. The purities of the samples were also checked by comparing the measured density data with those reported in the literature.

Table 1 reports the origins and density values of the chemicals, together with comparison with literature and stated purities from GCL analysis.

Calorimetric Measurements. The excess molar enthalpies H_{m}^{E} were determined with an LKB flow microcalorimeter (LKB Produkter, model 2107, Bromma, Sweden) equipped with two automatic burets (ABU, Radiometer, Copenhagen, Denmark) which pump liquids into the mixing cell of the calorimeter.

Details of the equipment, electrical calibration, and experimental procedure have been described previously (Monk and Wadso, 1968; Francesconi and Comelli, 1986).

The temperature inside the equilibrium cell was been measured by means of an electronic unit, and the mole fraction x_1 of diethyl carbonate (component 1) was determined from flow rates.

The estimated errors are $\delta x_1 < 0.0002$ and $\delta T/K = 0.01$ (Francesconi and Comelli, 1998).

Prior to measurements, the apparatus was checked against hexane + cyclohexane (Gmehling, 1993) and hexane + tetrachloromethane (Grolier et al., 1975), the agreement with the data reported in the literature being better than 0.5% over the central range of composition.

Volumetric Measurements. The excess molar volumes $V_{\rm m}^{\rm E}$ for the binary mixtures were determined from the densities ρ using a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) whose operating procedure has been described previously (Fermeglia and Lapasin, 1988). All the measurements were made at a constant temperature using an external ultrathermostat bath circulator (Heto, type 01 DBT 623, Birkeròd, Denmark), precision ± 0.005 K, and temperatures were detected with two digital thermometers (Anton Paar, DT-25, DT-40). Densities were measured with an accuracy of 1×10^{-5} g·cm⁻³, leading to

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Tuble 1. Source, I write, Densit, (p), and comparison with Enterature Data of I are Enquite	Table 1.	Source,	Purity,	Density	(p)	and Com	parison wi	ith I	Literature	Data	of Pu	re Lic	juids
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	ρ/(g·cm ⁻³)			
		this	lit.	
compound	source and purity	T/K = 298.15	T/K = 313.15	T/K = 298.15
diethyl carbonate	Aldrich, 99.8%	0.969 26	0.952 30	0.969 26 ^a
				$0.969\ 25^{b}$
2-methoxyethanol	Aldrich, +99.9%	0.960 04	0.946 11	$0.960~24^{a}$
U U				0.960 15 ^c
				$0.96 \ 00^{d}$
2-ethoxyethanol	Fluka, +99.5%	0.925 05	0.911 30	0.925 20 ^a
2-butoxyethanol	Fluka, +99.8%	0.896 31	0.883 61	0.896 25 ^a
2-(2-methoxyethoxy)ethanol	Aldrich, 99%	1.015 91	1.002 60	1.01 67 ^a
				1.01 64 ^e
				$1.014\ 87^{f}$
2-(2-ethoxyethoxy)ethanol	Aldrich. +99%	0.984 29	0.970 91	$0.98 \ 41^d$
× 5 5,	,			$0.98 \ 39^{e}$
2-(2-butoxyethoxy)ethanol	Aldrich. +99%	0.948 08	0.935 48	$0.94~79^{e}$
(Julie Juli	· · , · · · ·			0 949 16 ^d

^a Riddick et al., 1986. ^b Francesconi et al., 1997. ^c Rubio et al., 1998. ^d Cobos et al., 1989. ^e Pal and Sharma, 1998. ^f Cobos et al., 1988.



Figure 1. Experimental excess molar enthalpies $H_{\rm m}^{\rm E}$ for diethyl carbonate (1) + 2-methoxyethanol (2) (\blacksquare , \Box), + 2-ethoxyethanol (2) (\blacktriangle , \bigtriangleup), and + 2-butoxyethanol (2) (\blacklozenge , \bigcirc). Closed and open points are at (298.15 and 313.15) K, respectively.



Figure 2. Experimental excess molar enthalpies H_m^E for diethyl carbonate (1) + 2-(2-methoxy)ethanol (2) (\blacksquare , \Box), + 2-(ethoxyethoxy)ethanol (2) (\blacktriangle , \triangle) and + 2-(2-butoxyethoxy)ethanol (2) (\bullet , \bigcirc). Closed and open points are at (298.15 and 313.15) K, respectively.

 $V_{\rm m}^{\rm E}$ values with an error of ± 0.003 cm³·mol⁻¹. Mole fractions x_1 of diethyl carbonate were determined by mass using a Mettler balance (type AE 160) with an accuracy of ± 0.0001 g, charging the heavier component first to minimize the error due to vaporization and following the same procedure described by Fermeglia and Lapasin (1988). Corrections were made for buoyancy and evaporation of the



Figure 3. Experimental excess molar volumes $V_{\rm m}^{\rm E}$ for diethyl carbonate (1) + 2-methoxyethanol (2) (\blacksquare , \Box), + 2-ethoxyethanol (2) (\blacktriangle , \triangle) and + 2-butoxyethanol (2) (\bigstar , \triangle). Closed and open points are at (298.15 and 313.15) K, respectively.

components, but only the fourth decimal digit was affected. The technique was checked by determining $V_{\rm m}^{\rm E}$ for a benzene + cyclohexane mixture at 298.15 K. Our results are in good agreement with literature values (Wilhelm, 1985), showing a discrepancy of $\pm 0.5\%$ in the central range of mole fractions of benzene.

Results and Discussion

Excess molar volumes $V_{\rm m}^{\rm E}$ were computed from densities of mixtures ρ using the relation

$$V_{\rm m}^{\rm E} = (x_1 M_1 + x_2 M_2)/\rho - x_1 M_1/\rho_1 - x_2 M_2/\rho_2 \qquad (1)$$

where M_i and ρ_i are the molar mass and density of component *i*.

Excess molar enthalpies $H_{\rm m}^{\rm E}$ and excess molar volumes $V_{\rm m}^{\rm E}$ are listed in Tables 2 and 3, respectively.

Experimental data have been correlated as a function of composition using the Redlich–Kister polynomial

$$Q_{\rm m}^{\rm E} = x_1 x_2 \sum_{k \ge 0} A_k (x_1 - x_2)^k \tag{2}$$

where $Q_m^E = H_m^E / J \cdot mol^{-1}$ or $V_m^E / cm^3 \cdot mol^{-1}$, x_1 and x_2 are the

Table 2. Experimental Excess Enthalpies H^{E}_{m} , of Diethyl Carbonate + *n*-Alkoxy- and *n*-(Alkoxyethoxy)ethanols at (298.15 and 313.15) K

<i>X</i> 1	$H_{ m m}^{ m E}/$ J \cdot mol $^{-1}$	<i>X</i> 1	$H_{\mathrm{m}}^{\mathrm{E}}/\mathrm{J}\cdot\mathrm{mol}^{-1}$	<i>X</i> 1	$H_{ m m}^{ m E}/$ J·mol ⁻¹	<i>X</i> 1	$H_{\mathrm{m}}^{\mathrm{E}}/$ J·mol ⁻¹	<i>X</i> 1	$H_{ m m}^{ m E}/$ J \cdot mol $^{-1}$	<i>X</i> 1	$H_{\mathrm{m}}^{\mathrm{E}}$ / J·mol ⁻¹
				diethyl cai	rbonate (1) +	- 2-methoxy	yethanol (2)				
					T/K =	298.15					
0.0264	80	0.2454	642	0.7223	914	0.0978	281	0.4939	964	0.8864	539
0.0514	152	0.3023	746	0.7960	788	0.1398	407	0.5653	993	0.9398	321
0.0752	221	0.3941	881	0.8388	688	0.1781	498	0.6611	964		
					T/K =	313.15					
0.0263	94	0.2448	747	0.7217	1033	0.0975	334	0.4931	1123	0.8861	595
0.0512	183	0.3017	8/2	0.7955	885	0.1395	468	0.5646	1147	0.9396	352
0.075	234	0.3933	1028	0.0304	703		J75	0.0005	1110		
				diethyl ca	rbonate (1)	+ 2-ethoxy	ethanol (2)				
0.0000		0.0055	~	0 7040	T/K =	298.15	0.0 5	0 5 4 5 4	0.70	0.0050	100
0.0322	94	0.2855	714	0.7618	844	0.1175	335	0.5454	979	0.9056	466
0.0024	260	0.3470	931	0.8275	607	0.1000	570	0.0252	982 924	0.9303	210
0.0000	200	0.1112	001	0.0010		010 15	010	0.1001	021		
0.0321	117	0 2850	831	0 7613	1/K = 0.000	0 1173	398	0 5447	1128	0 9054	518
0.0623	222	0.3469	946	0.8271	808	0.1662	535	0.6146	1120	0.9503	300
0.0906	315	0.4436	1072	0.8645	692	0.2099	662	0.7052	1062		
				diethyl c	arbonate (1)	+ butoxye	thanol (2)				
				J	7/K =	208 15					
0.0431	159	0.3510	959	0.8123	846	0.1527	517	0.6138	1117	0.9285	416
0.0827	296	0.4189	1047	0.8665	665	0.2129	681	0.6839	1084	0.9629	231
0.1191	410	0.5196	1122	0.8964	560	0.2650	800	0.7644	950		
					$T/\mathbf{K} = \mathbf{k}$	313.15					
0.0430	168	0.3503	1062	0.8118	911	0.1523	570	0.6180	1235	0.9283	444
0.0824	318	0.4181	1163	0.8661	723	0.2123	742	0.6832	1176	0.9228	248
0.1188	448	0.5188	1237	0.8961	596	0.2644	890	0.7639	1027		
			dietł	ıyl carbona	te $(1) + 2 - (2)$	-methoxyet	thoxy)ethano	ol (2)			
					T/K =	298.15					
0.0388	73	0.3267	529	0.7951	630	0.1392	251	0.5929	737	0.9209	346
0.0748	141	0.3927	612	0.8534	521	0.1952	346	0.6600	733	0.9588	197
0.1082	201	0.5075	699	0.8859	456	0.2444	429	0.7443	692		
0.0007		0.0057	057	0 70 4 4	T/K = 1	313.15		0 5040	0.0 5	0.0404	
0.0387	84	0.3257	657	0.7944	775	0.1386	309	0.5918	895	0.9164	440
0.0745	104 941	0.3910	747 846	0.8329	555	0.1945	421 521	0.0589	842	0.9367	244
0.1077	211	0.1011	diat	bul conhon	ata $(1) \perp 2$	othorwoth	o≈1	(9)	012		
			ulet	Inyi carbon	ate (1) $\pm 2-0.00$	c-ethoxyeth	ioxy)ethanoi	(2)			
0.0445	65	0.2507	594	0 0179	T/K = 500	298.15	957	0 6966	707	0 0207	919
0.0445	131	0.3387	534 611	0.8173	495	0.1371	350	0.0200	707	0.9307	178
0.1227	192	0.5280	684	0.8995	412	0.2716	426	0.7704	654	0.0011	170
					$T/\mathbf{K} =$	313 15					
0.443	83	0.3578	658	0.8167	698	0.1566	321	0.6257	846	0.9304	365
0.0849	168	0.4261	733	0.8699	582	0.2313	457	0.6902	828	0.9640	208
0.1222	240	0.5270	825	0.8991	488	0.2708	527	0.7697	771		
			diet	hyl carbon	ate $(1) + 2 - (2)$	2-butoxyetl	noxy)ethanol	(2)			
				5	7/K =	298 15	5.				
0.0553	91	0.4125	630	0.8488	549	0.1896	332	0.6781	734	0.9440	268
0.1047	181	0.4834	690	0.8939	437	0.2598	445	0.7374	703	0.9712	149
0.1493	251	0.5840	736	0.9182	370	0.3188	523	0.8081	628		
					T/K =	313.15					
0.0550	113	0.4114	733	0.8483	622	0.1889	397	0.6772	854	0.9438	299
0.1043	218	0.4823	809	0.8935	501	0.2590	519	0.7366	806	0.9711	164
U.1488	311	0.5830	858	0.9179	407	0.3179	625	0.8075	/16		

mole fractions of diethyl carbonate and component 2, and A_k are the adjustable parameters. The values of A_k have been obtained by a least-squares method with all points weighted equally. The parameters A_k and the standard deviation $\sigma(Q_{\rm m}^{\rm E})$ are listed in Table 4.

Figures 1-4 report all 24 mixtures. For the sake of clarity, we have represented graphically only the experimental points and not the Redlich–Kister curves, which in many cases overlap. Figures 1-3 show that all excess

values are positive over the whole range of composition, with the exception of the $V_{\rm m}^{\rm E}$ values represented in Figure 4, referring to mixtures containing (*n*-alkoxyethoxy)ethanols and showing an inversion of sign.

Figure 1 shows overlapping of $H_{\rm m}^{\rm E}$ data for binary mixtures of diethyl carbonate with 2-methoxyethanol and 2-ethoxyethanol, whereas 2-butoxyethanol gives values 10% greater. The same trend is observed at (298.15 and 313.15) K.

Table 3.	Densities ρ and	Experimental	Excess	Volumes,	V_{m}^{E} of Diethyl	Carbonate +	<i>n</i> -Alkoxy- and
<i>n</i> -Alkoxy	ethoxyethanols	at (298.15 and	313.15)	K			Ũ

		$V_{\rm m}^{\rm E}/{\rm cm^3}$			$V_{\rm m}^{\rm E}/{\rm cm^{3}}$			$V_{\rm m}^{\rm E}/{\rm cm^{3}}$			$V_{\rm m}^{\rm E}/{\rm cm^3}$
X_1	$ ho/{ m g}{\cdot}{ m cm}^{-3}$	mol^{-1}	<i>X</i> ₁	$ ho/g\cdot cm^{-3}$	mol ⁻¹	<i>X</i> 1	$ ho/g \cdot cm^{-3}$	mol^{-1}	X_1	$ ho/{ m g}{\cdot}{ m cm}^{-3}$	mol^{-1}
				diethyl carbo	nate (1) +	2-methoxye	thanol (2)				
					T/K = 2	98.15					
0.0363	0.960 25	0.024	0.4686	0.963 30	0.210	0.2656	0.961 78	0.147	0.7641	0.966 04	0.195
0.0879	0.960 58	0.056	0.5319	0.963 83	0.220	0.3182	0.962 16	0.168	0.7995	0.966 45	0.179
0.1578	0.961 04	0.095	0.6023	0.964 44	0.223	0.3500	0.962 39	0.179	0.8638	0.967 22	0.141
0.2145	0.301 43	0.124	0.0370	0.303 34	U.214	10.15	0.302 33	0.200	0.3122	0.307 87	0.101
0.0363	0 9/6 18	0.023	0.4686	0 947 35	T/K = 3 0.248	13.15	0.946.60	0.164	0 7641	0 949 43	0 221
0.0879	0.946 29	0.025	0.5319	0.947 68	0.259	0.3182	0.946 79	0.191	0.7995	0.949 78	0.201
0.1578	0.946 42	0.100	0.6023	0.948 11	0.263	0.3500	0.946 89	0.205	0.8638	0.950 49	0.153
0.2143	0.946 53	0.134	0.6976	0.948 83	0.247	0.4224	0.947 18	0.231	0.9122	0.951 09	0.107
				diethyl carb	onate (1) +	2-ethoxyet	hanol (2)				
					T/K = 2	98.15					
0.0418	0.927 10	0.026	0.5248	0.948 85	0.215	0.3110	0.939 60	0.157	0.7783	0.959 47	0.192
0.1202	0.930 87	0.068	0.5889	0.951 54	0.221	0.3643	0.941 95	0.176	0.8084	0.960 74	0.179
0.1775	0.933 56	0.097	0.6474	0.953 98	0.221	0.4085	0.943 87	0.191	0.9025	0.964 80	0.116
0.2520	0.936 97	0.132	0.7004	0.956 20	0.214	0.4827	0.947 06	0.208	0.9629	0.967 51	0.052
0.0410	0.010.17	0.000	0 5040	0.000.07	T/K = 3	13.15	0.004 50	0.107	0 7700	0.040.00	0.000
0.0418	0.913 17	0.028	0.5248	0.932 97	0.258	0.3110	0.924 50	0.187	0.7783	0.942 90	0.228
0.1202	0.919 03	0.113	0.6474	0.937 76	0.261	0.4085	0.928 43	0.224	0.9025	0.948 01	0.134
0.2520	0.922 11	0.157	0.7004	0.939 81	0.256	0.4827	0.931 33	0.248	0.9629	0.950 64	0.057
				diethyl carb	onate $(1) +$	2-hutovvet	hanol (2)				
				ulculyi carb	T U = 0	~ Dutoxyeti					
0.0680	0 900 70	0.041	0 5123	0 930 67	1/K = 2 0.214	98.15	0.916.24	0 158	0.81/1	0 953 49	0 170
0.0089	0.900 70	0.041	05654	0.930.07	0.214	0.3051	0.910 24	0.138	0.8141	0.959.93	0.170
0.1880	0.908 45	0.103	0.6214	0.938 65	0.218	0.4276	0.924 68	0.100	0.9265	0.962 79	0.089
0.2375	0.911 71	0.129	0.6639	0.941 83	0.215	0.4851	0.928 73	0.210			
					T/K = 3	13.15					
0.0689	0.887 73	0.044	0.5123	0.915 71	0.253	0.3051	0.902 21	0.185	0.8141	0.937 25	0.199
0.1281	0.891 29	0.083	0.5654	0.919 34	0.256	0.3957	0.908 00	0.224	0.8928	0.943 39	0.138
0.1880	0.894 92	0.122	0.6214	0.923 20	0.258	0.4276	0.910 09	0.233	0.9265	0.946 11	0.102
0.2375	0.898 00	0.148	0.6639	0.926 22	0.252	0.4851	0.913 89	0.249			
			dieth	yl carbonate	(1) + 2 - (2 - 1)	nethoxyetho	oxy)ethanol (2)				
					T/K = 2	98.15					
0.0319	1.014 40	-0.003	0.5314	0.990 48	0.036	0.2541	1.003 76	0.004	0.7975	0.977 98	0.063
0.0651	1.012 82	-0.004	0.5699	0.988 64	0.042	0.2946	1.001 82	0.007	0.8898	0.97384	0.054
0.1234	1.010 03	-0.004	0.6378	0.985 43	0.050	0.3852	0.997 47	0.017	0.9310	0.972 06	0.042
0.1799	1.007 32	-0.001	0.0621	0.983 33	0.056	0.4110	0.996 20	0.020	0.9071	0.970 56	0.025
0.2101	1.000 01	0.001	0.1101	0.010 00	TW = 2	19.15	0.00111	0.020			
0.0319	1 000 98	-0.005	0 5314	0 97514	1/K = 3 0.038	0 2542	0 989 50	-0.002	0 7975	0 961 68	0 070
0.06511	0.999 28	-0.007	0.5699	0.973 16	0.045	0.2946	0.987 41	0.002	0.8898	0.957 13	0.060
0.1234	0.996 37	-0.008	0.6378	0.969 69	0.056	0.3852	0.982 71	0.014	0.9310	0.955 33	0.045
0.1799	0.993 37	-0.009	0.6821	0.967 45	0.061	0.4116	0.981 34	0.018	0.9671	0.953 72	0.025
0.2191	0.991 31	-0.004	0.7767	0.951 69	0.071	0.4555	0.979 06	0.025			
			diet	hyl carbonate	e(1) + 2-(2-	ethoxyetho	xy)ethanol (2)				
					T/K = 2	98.15					
0.0376	0.933 81	-0.004	0.5630	0.975 89	0.046	0.3288	0.979 64	0.009	0.8124	0.971 77	0.072
0.0965	0.983 03	-0.007	0.6131	0.975 06	0.054	0.3515	0.979 30	0.011	0.9011	0.970 43	0.059
0.1542	0.982 22	-0.006	0.6771	0.973 99	0.064	0.3915	0.978 68	0.016	0.9506	0.96979	0.036
0.2332	0.980 31	0.001	0.8007	0.973 32	0.073	0.4890	0.977 11	0.032	0.3720	0.303 34	0.022
					$T/\mathbf{K} = 3$	12 15					
0.0376	0.970.33	-0.007	0.5630	0.960.56	0.060	0.3288	0.965 14	0.014	0.8124	0.955 47	0.087
0.0965	0.969 35	-0.009	0.6131	0.959 49	0.069	0.3515	0.964 69	0.019	0.9011	0.953 82	0.071
0.1542	0.968 35	-0.007	0.6772	0.958 20	0.077	0.3915	0.963 92	0.025	0.9506	0.953 02	0.043
0.2391	0.966 81	0.001	0.7176	0.957 37	0.084	0.4728	0.962 32	0.041	0.9728	0.952 69	0.026
0.2849	0.965 96	0.007	0.8007	0.955 70	0.088	0.4890	0.962 00	0.045			
			diet	hyl carbonate	e(1) + 2 - (2 -)	butoxyetho	xy)ethanol (2)				
					T/K = 2	98.15					
0.0880	0.949 46	-0.003	0.7118	0.961 23	0.051	0.450 71	0.956 88	0.024	0.9299	0.966 93	0.040
0.1518	0.950 51	-0.006	0.7668	0.962 52	0.056	0.5249	0.957 24	0.026	0.9633	0.967 99	0.026
0.2932	0.952 92	-0.002	0.8246	0.963 97	0.057	0.6202	0.959 19	0.041	0.9788	0.968 52	0.016
0.3000 0.4433	0.954 Z3 0 955 66	0.006	U.8/81 0 9097	0.905 42	0.052	0.0008	0.900 21	0.047			
0.7700	0.000 00	0.014	0.3027	0.000 12	717 0	10.17					
0 0880	0 026 61	-0.000	0 7119	0 945 82	1/K = 3 0.050	13.15 0 5071	0 949 44	0 097	0 0200	0 950 20	0.049
0.1518	0.937 47	-0.014	0.7668	0.946 85	0.063	0.5249	0.942 71	0.027	0.9633	0.951 27	0.042
0.2932	0.939 35	-0.003	0.8246	0.948 01	0.062	0.6202	0.944 24	0.046	0.9788	0.951 70	0.015
0.3666	0.940 37	0.005	0.8781	0.949 16	0.056	0.6668	0.945 04	0.052			
0.4433	0.091 48	0.017	0.9027	0.949 73	0.051						

Table 4. Least-Squares Parameters a_k and Standard Deviations $\sigma(Q_m^E)$ of Diethyl Carbonate + Alkoxyethanols at (298.15 and 313.15) K

function	a_0	a_1	a_2	a_3	a_4	$\sigma(Q_{\rm m}^{\rm E})$				
dieth	ıyl carbo	nate (1)	+ 2-metł	noxyetha	nol (2)					
E .		T/K =	298.15							
$H_{\rm m}^{\rm E}$ /J·mol ⁻¹	3888.2	1053.1	729.4	482.6		3.6				
$V_{ m m}^{ m E}/ m cm^3\cdot mol^{-1}$	0.8620	0.3001	0.1770	0.0690		0.0009				
		T/K =	313.15							
$H_{ m m}^{ m E}/ m J\cdot mol^{-1}$	4513.9	1095.7	576.0	393.1		2.7				
$V_{\rm m}^{\rm E}/{\rm cm^3 \cdot mol^{-1}}$	1.0174	0.3881				0.0008				
diet	hyl carb	onate (1)	+ 2-ethe	oxyethan	nol (2)					
		T/K =	298.15							
$H_{\rm m}^{\rm E}/{\rm J}\cdot{\rm mol}^{-1}$	3865.0	1010.6	682.5			3.7				
$V_{\rm m}^{\rm E}/{\rm cm^3 \cdot mol^{-1}}$	0.8432	0.3500	0.1988	0.1163		0.0009				
- III -		7/K =	313.15							
$H^{\rm E}/J\cdot {\rm mol}^{-1}$	4465.8	1170.2	754.7	361.3		3.7				
$V^{E}/cm^{3}\cdot mol^{-1}$	1.0064	0.4181	0.1792	0.1277		0.0014				
diet	hvl carb	onate (1)	+ 2-but	oxvethar	nol (2)					
$T/K = 208 \ 15$										
$H^{\rm E}/\rm I\cdot mol^{-1}$	4457.9	1032.8	811.4	439.2		4.5				
$V^{E}/cm^{3} \cdot mol^{-1}$	0.8443	0.3018	0.1620	0.1279		0.0012				
$v_{\rm m}$ /cm more 0.0010 0.0010 0.1273 0.0012										
$H^{\rm E}/\rm{I-mol}^{-1}$	4932.4	997 8	661.6	580 5		4 1				
$V_{\rm m}^{\rm E}/{\rm cm^3 \cdot mol^{-1}}$	1 0010	0.3018	0 1620	0 1279		0.0012				
diothyl co	rhonata	$(1) \pm 2$	2 mothor	avothova) other of	(2)				
uletilyi ta	Donate	(1) + ~-(A	2-IIIetii02	yethoxy	Jethanoi	(2)				
TE/T = al-1	9791 5	1/K =	= 298.15 906 5	5211		4.4				
$H_{\rm m}/J^{\bullet}$ [110] I	£701.5 0 1250	0 2651	0 2115	0 1079		4.4				
	0.1250	0.2031	0.2115	0.1572		0.0008				
τνΕ/τ 1−1	9409 1	I/K =	313.15	019 1		16				
$H_{\rm m}^{-}/J \cdot {\rm mol}^{-1}$	0 1970	1429.0	909.0	013.1		1.0				
$V_{\rm m}^{-}/{\rm cm^{3} \cdot mol^{-1}}$	0.1270	0.3309	0.2094	0.1905		0.0008				
diethyl c	arbonate	e(1) + 2-	(2-ethoxy	yethoxy)	ethanol(2)				
F		T/K =	= 298.15							
$H_{\rm m}^{\rm E}/{ m J}{ m \cdot mol^{-1}}$	2652.6	1251.5	787.5	824.7		3.4				
$V_{\rm m}^{\rm E}/{ m cm^3 \cdot mol^{-1}}$	0.1367	0.3395	0.2269	0.1766		0.0009				
		T/K =	= 313.15							
$H_{\underline{\mathrm{m}}}^{\mathrm{E}}/\mathrm{J}{\cdot}\mathrm{mol}^{-1}$	3198.6	1354.3	914.8	985.2		4.2				
$V_{\rm m}^{\rm E}/{ m cm^3\cdot mol^{-1}}$	0.1844	0.3861	0.2261	0.2603		0.0010				
diethyl c	arbonate	e (1) + 2-	(2-butoxy	yethoxy)	ethanol ((2)				
		T/K =	= 298.15							
$H_{ m m}^{ m E}/{ m J}{ m \cdot}{ m mol}^{-1}$	2796.9	1208.2	769.8	853.8		3.4				
$V_{-}^{E}/cm^{3}\cdot mol^{-1}$	0.0920	0.2865	0.1186	0.1206	0.1966	0.0007				

3.9
0.0007

Due to hydrogen bonding, the maximum values of $H_{\rm m}^{\rm E}$ are all over 1000 J·mol⁻¹ with an increase of $H_{\rm m}^{\rm E}$ with increasing temperature.

A different pattern results for the $H_{\rm m}^{\rm E}$'s of the mixtures diethyl carbonate + 2-(2-alkoxyethoxy)ethanols, as given in Figure 2. Here, the values of the $H_{\rm m}^{\rm E}$ maxima are smaller than the ones of alkoxyethanols of Figure 1, with the same temperature dependence.

In conclusion, the increased number of alkoxy groups linearly chained to ethanol seems to decrease the heat of mixing with diethyl carbonate, the differences among

various (alkoxyethoxy)ethanols being very small. As to the V_m^E data, the curves of V_m^E versus x_1 for both the 2-alkoxyethanols and (2-alkoxyethoxy)ethanols practically overlap, with larger values displayed by the former mixtures, whereas the latter mixtures show a sign inver-



Figure 4. Experimental excess molar volumes V_m^E for diethyl carbonate (1) + 2-(2-methoxyethoxy)ethanol (■, □), + 2-(2-ethoxyethoxy)ethanol (2) (\blacktriangle , \triangle), and + 2-(2-butoxyethoxy)ethanol (2) (\bigcirc , O). Closed and open points are at (298.15 and 313.15) K, respectively.

sion in the $V_{\rm m}^{\rm E}$ versus data x_1 in the diethyl carbonate-poor region.

The temperature dependence of V_m^E is again positive but more marked than that for the H_m^E data. It must be pointed out that the 2-alkoxyethanols studied in this paper show V_m^E curves with sign inversion in mixtures with trichloroethylene and similar to Figure 3 in mixtures with tetrachloroethylene (Venkatesulu and Rao, 1992).

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