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Thermodynamics of Binary Mixtures Containing Ethers or Acetals. 1. Excess Enthalpies of Linear Ethers or Acetals + Heptane or + Cyclohexane Mixtures

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A Tian-Calvet type calorimeter has been used to determine molar excess enthalpies, H^E, as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing linear mono- or polyethers or acetals with heptane or cyclohexane. The experimental H^E results are interpreted in terms of oxygen/alkyl interchange enthalpies by using equations derived from the group surface interaction version of Guggenheim's lattice theory in the zeroth approximation. There is clear evidence for steric effect exerted by *n*-alkyl groups adjacent to the –O– and for "proximity effect" in compounds containing the $-O-CH_2-O-$ group (acetals).

Introduction

This work is part of a systematic study of the thermodynamic properties of liquid organic mixtures, T.O.M. Project (*1–3*), with the purpose of developing accurate group contribution models used to predict thermodynamic excess functions, molar excess Gibbs energy, G^E, and molar excess enthalpy, H^E.

Mono- and poly(oxaalkanes) of general formula

$$CH_3(CH_2)_{m-1}-O-[(CH_2)_u-O-]_{v-1}-(CH_2)_{n-1}CH_3$$

represent, besides a technically important class of substances, a particularly interesting class of molecules for the purpose of testing group contribution models. Indeed, these molecules are formally obtained by replacing one or several $-CH_2-$ groups in an *n*-alkane by –O– atoms.

A large variety of homomorphic molecular species are thus obtained which differ by the number and relative positions of the same functional group, –O–, but have the same chain structure.

Three classes deserve special attention:

(A) $CH_3(CH_2)_{m-1}-O-(CH_2)_{n-1}CH_3$ monoethers

(B) $CH_3-O-CH_2-O-CH_3$

$CH_3CH_2-O-CH_2-O-CH_2CH_3$ acetals

(C) $CH_3-O-(CH_2CH_2-O-)_{v-1}-CH_3$

$CH_3CH_2-O-(CH_2CH_2-O-)_{v-1}-CH_2CH_3$ polyoxyethylenes

Class A serves to study the steric effect of alkyl groups, class B the proximity effect of two –O– groups, and class C the effect of an increasing number of oxyethylene groups on the model parameters.

Mixtures of each of these classes of compounds with *n*-alkanes have been successfully interpreted in terms of the quasi-lattice group contribution theory in the zeroth approximation (*4–9*). More recent studies (*10–14*) confirmed the previous results, but also revealed systematic discrepancies between the experimental and the predicted H^E curves.

The purpose of this work was to provide additional experimental H^E data for mixtures with *n*-alkanes and to study mixtures of the same oxygen compounds with cyclohexane. A literature search revealed indeed little data on mono- or polyethers or acetals with cyclohexane.

Experimental Section

The excess enthalpies, H^E, were measured with a Tian-Calvet ("CRMT") type calorimeter which was manually tilted. The batch mixing cell and the experimental procedure are reported in the literature (*15*). The calorimeter was calibrated by the Joule effect and the calibration was repeated after each experiment. Comparison of measurements for the benzene + cyclohexane system with literature data (*16*) indicated that the precision of our results is 2%. All measurements were made at an average temperature of 298.15 ± 0.10 K. The experimental values, H^E, reported in Tables I–III and represented in part in Figures 1–3, were fitted to the smoothing equation

$$H^E/\text{J mol}^{-1} = x_1 x_2 \sum a_i (x_1 - x_2)^i \qquad (1)$$

where x_1 is the mole fraction of ether and x_2 that of *n*-heptane or cyclohexane. Values for the standard deviations $\sigma(H^E)$ are given by

$$\sigma(H^E) = [\sum (H^E_{sm} - H^E_{exptl})^2/(N - n)]^{1/2} \qquad (2)$$

where N is the number of experimental points and n is the number of coefficients a_i. The values for the coefficients a_i, eq 1, and the standard deviations $\sigma(H^E)$, eq 2, determined by least squares, are reported in Tables IV–VI.

Literature data are available for heptane + butyl methyl ether (*5*), + dipropyl ether (*11*, *17*), + dibutyl ether (*4*, *18*, *19*), + 2,4-dioxapentane (*20*, *21*), + 2,5-dioxahexane (*5*, *14*, *17*), + 3,5-dioxaheptane (*20*, *21*), + 3,6-dioxaoctane (*5*, *13*, *17*), + 2,5,8-trioxanonane (*5*, *12*, *17*), and + 3,6,9-trioxaundecane (*5*).

Our H^E data are in good agreement (within 2% in the central range of concentration) with the measurements by Benson and

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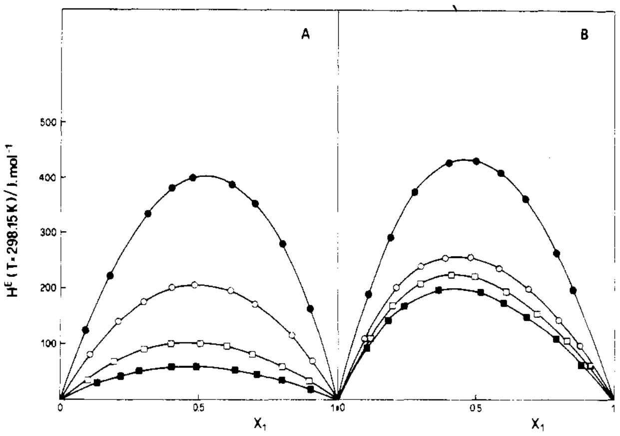

Figure 1. Experimental excess enthalpies H^E at 298.15 K of monoethers + heptane (A) or + cyclohexane (B) mixtures versus x_1, the mole fraction of monoether: ●, diethyl ether; ○, dipropyl ether; □, dibutyl ether; ■, dipentyl ether.

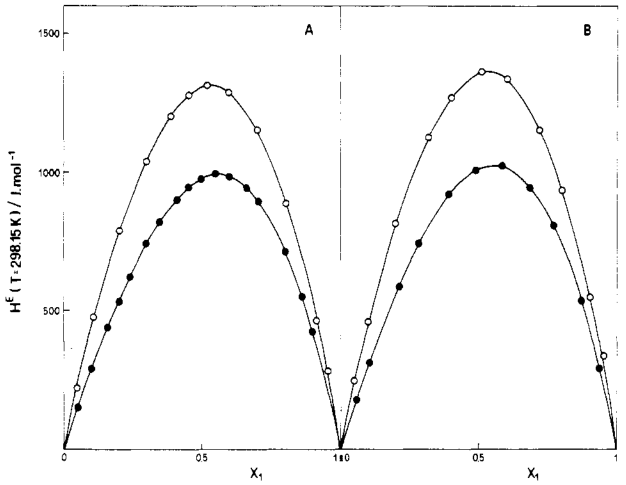

Figure 2. Experimental excess enthalpies H^E at 298.15 K of dioxaalkanes + heptane (A) or + cyclohexane (B) mixtures versus x_1, the mole fraction of dioxaalkane: ●, 2,4-dioxapentane; ○, 2,5-dioxahexane.

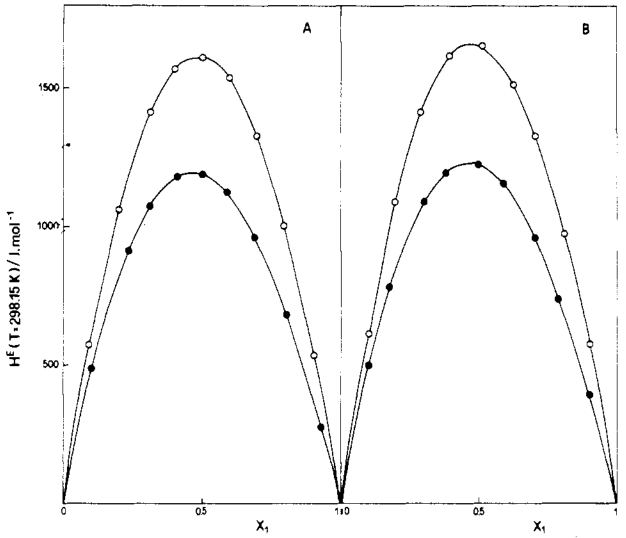

Figure 3. Experimental excess enthalpies H^E at 298.15 K of polyethers + heptane or + cyclohexane (B) mixtures versus x_1, the mole fraction of polyether: ○, 2,5,8-trioxanonane; ●, 3,6,9-trioxaundecane.

co-workers (*17*), which are probably the most reliable, and the same good agreement is obtained with the other data.

Literature data are available for cyclohexane + diethyl ether (*22*), + dipropyl ether (*23*), and + 2,5-dioxahexane (*23*) only.

Table I. Experimental Values of the Excess Enthalpies, H^E, for Binary Mixtures of Monoethers (1) with Heptane (2) or Cyclohexane (2) at 298.15 K

with heptane (2)		with cyclohexane (2)	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
	Diethyl Ether (1)		
0.0875	124	0.1102	190
0.1803	222	0.1875	295
0.3144	332	0.2800	376
0.4089	385	0.3997	424
0.4747	400	0.5033	433
0.6212	391	0.5912	411
0.7050	352	0.6794	366
0.7996	280	0.7918	263
0.9000	166	0.8506	200
	Butyl Methyl Ether (1)		
0.110	122	0.1212	176
0.2077	200	0.2100	264
0.2870	256	0.3197	332
0.3952	299	0.4023	357
0.4964	314	0.4855	364
0.6021	302	0.6348	320
0.6956	268	0.7590	238
0.8084	201	0.8206	184
0.9215	97	0.9004	105
	Butyl Ethyl Ether (1)		
0.1205	93	0.1094	120
0.2072	144	0.2106	191
0.2938	173	0.3077	233
0.4011	200	0.4152	250
0.4957	206	0.5033	247
0.5988	202	0.6122	222
0.7245	168	0.7038	187
0.8126	131	0.7929	144
0.9049	76	0.9114	70
	Dipropyl Ether (1)		
0.1083	80	0.0936	112
0.2100	138	0.2115	198
0.2975	176	0.3008	239
0.4041	200	0.3921	256
0.4833	205	0.4838	258
0.6108	196	0.5800	235
0.7006	172	0.6907	200
0.8314	115	0.8025	144
0.9007	70	0.8744	95
	Dibutyl Ether (1)		
0.0919	38	0.1145	112
0.1945	68	0.1970	170
0.2978	87	0.3000	209
0.4010	99	0.4121	226
0.6013	94	0.4931	220
0.6916	80	0.6077	196
0.8020	59	0.7222	155
0.9005	33	0.8316	104
		0.9090	62
	Dipentyl Ether (1)		
0.1324	31	0.0996	94
0.2145	44	0.1794	143
0.2817	52	0.2410	170
0.4032	59	0.3652	197
0.4911	60	0.5145	192
0.6276	53	0.5977	175
0.7061	46	0.6803	150
0.8002	35	0.7900	111
0.9044	18	0.8788	63

Our H^E data agree to within 2% in the central range of concentration with the measurements of Arm et al. (*22*), but differ by as much as 10% or more from the data reported by De Torre et al. (*23*) at 303.15 K.

Discussion

The substitution of a $-CH_2-$ group in an *n*-alkane with an $-O-$ atom influences the intermolecular forces as a result of two

Table II. Experimental Values of the Excess Enthalpies, H^E, for Binary Mixtures of Acetals (1) + Heptane (2) or Cyclohexane (2) at 298.15 K

with heptane (2)		with cyclohexane (2)	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
	2,4-Dioxapentane (1)		
0.0495	154	0.0559	176
0.0983	291		
0.1576	441	0.1032	313
0.1968	534	0.2113	589
0.2400	628	0.2829	745
0.2997	745	0.3935	923
0.3451	821	0.4859	1007
0.4088	907	0.5762	1030
0.4473	945	0.6864	950
0.4902	975	0.7668	815
0.5474	993	0.8710	538
0.6013	982	0.9374	291
0.6620	944		
0.7024	896		
0.8016	715		
0.8635	550		
0.9006	429		
	3,5-Dioxaheptane (1)		
0.0597	134	0.1015	228
0.1011	216	0.2081	409
0.2002	376	0.2940	525
0.3018	501	0.4077	620
0.3995	577	0.4995	646
0.5024	610	0.6200	618
0.6041	589	0.7012	557
0.6973	525	0.8233	400
0.8072	396	0.9008	250
0.9034	230		
0.9447	140		

oppositely acting effects, one, weakening, due to smaller dispersion forces exerted by the –O– atoms, compared to the –CH_2– groups, and another, strengthening, due to electrostatic interactions between the C–O bond dipoles (*4*). The latter being relatively weak, the amount of order in the liquid phase is rather small. Thus, ether + alkane mixtures could be described fairly well by a pseudolattice group contribution model in the zeroth (random mixing) approximation (*5*, *7*, *9*).

Three kinds of contact surfaces were distinguished on the molecules investigated in this work: (a) aliphatic (CH_3 and CH_2), (c) cyclohexane (C_6H_{12}), and (e) oxygen (O). The total relative contact surface, q_i, of molecule of type i (ether, acetal, or alkane) and the oxygen surface fraction, α_{1e}, on a molecule of type 1 (ether or acetal) were calculated from the relative group surfaces (*7*, *24*): $q_{CH_3} = 0.73103$, $q_{CH_2} = 0.46552$, $q_{C_6H_{12}} = 2.59660$, $q_O = 0.20690$. According to the model, H^E is given by

$$H^E/RT = \frac{q_1 q_2 x_1 x_2}{q_1 x_1 + q_2 x_2} h_{12}/RT \qquad (3)$$

where h_{12} is the overall molar interaction enthalpy, a parameter which depends on the molecular structure of the components but not on the composition.

For ether or acetal + cyclohexane mixtures, h_{12}/RT is given by (*5*)

$$h_{12}/RT = C_{ae,2}\alpha_{1e}^2 - (C_{ac,2} + C_{ae,2} - C_{ce,2})\alpha_{1e} + C_{ac,2} \qquad (4)$$

where $C_{st,2}$ is the enthalpy of interchange between contact surfaces of type s and t (s, t = a, c, or e).

For ether or acetal + *n*-alkane mixtures

$$h_{12}/RT = C_{ae,2}\alpha_{1e}^2 \qquad (5)$$

and for cyclohexane + *n*-alkane mixtures

$$h_{12}/RT = C_{ac,2} \qquad (6)$$

Table III. Experimental Values of the Excess Enthalpies for Binary Mixtures of Polyethers (1) + Heptane (2) or Cyclohexane (2) at 298.15 K

with heptane (2)		with cyclohexane (2)	
x_1	H^E/J mol^{-1}	x_1	H^E/J mol^{-1}
	2,5-Dioxahexane (1)		
0.0461	217	0.0503	245
0.1084	475	0.1001	461
0.2016	792	0.1998	812
0.2972	1038	0.3196	1124
0.3858	1199	0.4000	1268
0.4550	1277	0.5112	1358
0.5236	1308	0.5996	1335
0.5969	1287	0.7213	1152
0.7037	1148	0.7995	937
0.8018	889	0.8984	550
0.9093	463	0.9593	240
0.9474	279		
	3,6-Dioxaoctane (1)		
0.0914	286	0.0997	320
0.2066	573	0.1889	560
0.2873	719	0.2935	760
0.4018	845	0.3742	853
0.5105	874	0.4906	908
0.6087	828	0.6037	865
0.7079	714	0.7103	751
0.8171	515	0.8050	572
0.9160	267	0.9008	324
	2,5,8-Trioxanonane (1)		
0.0932	577	0.0992	616
0.1973	1061	0.1950	1087
0.3104	1416	0.2897	1415
0.3978	1572	0.3936	1617
0.4979	1622	0.5094	1655
0.5982	1543	0.6258	1514
0.7001	1336	0.7065	1328
0.8029	1011	0.8111	976
0.9096	539	0.9003	576
	3,6,9-Trioxaundecane (1)		
0.1031	491	0.0994	500
0.2336	920	0.1767	786
0.3078	1074	0.2988	1087
0.4100	1185	0.3800	1193
0.5024	1194	0.5005	1224
0.5899	1123	0.5923	1154
0.6892	965	0.7061	960
0.8058	684	0.7919	740
0.9326	270	0.8985	392
	2,5,8,11-Tetraoxadodecane (1)		
0.0999	709	0.1006	733
0.1997	1215	0.1988	1246
0.3002	1537	0.3015	1586
0.4005	1693	0.3970	1740
0.5008	1704	0.5000	1755
0.5982	1589	0.6012	1628
0.6986	1347	0.6994	1384
0.7997	985	0.8009	1012
0.8893	574	0.9021	535

According to the group contribution model, the $C_{st,2}$ coefficients should depend on the type of contact surfaces (or groups) only and should be independent of the type of molecules. This is usually not exactly the case, in part because of the inadequacy of the underlying theoretical model and in part because of additional inter- or intramolecular effects.

(a) Mixtures of Linear Mono- or Polyethers with n-Alkanes. Using the previously reported average value for the interchange coefficient of the a,e contact, $C_{ae,2}$(av) = 29.0 (*5*)

$$h_{12}/RT = 29.0\alpha_{1e}^2 \quad \text{(mono- or polyethers + } n\text{-alkanes)} \qquad (7)$$

we calculate H^E's for all the investigated mono- or polyether + *n*-alkane systems (Tables I and III) to within 100 J mol^{-1}, except for 2,5,8,11-tetraoxadodecane + heptane, where the

Table IV. Values for the Coefficients a_i, Eq 1, and the Standard Deviation $\sigma(H^E)$, Eq 2, for the Binary Systems Monoethers (1) with Heptane (2) or Cyclohexane (2) at 298.15 K

ether	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$/ J mol^{-1}
diethyl ether (1) +						
C_7H_{16} (2)	1624	185	−117	23	348	2.4
C_6H_{12} (2)	1728	−198	254	−160	−431	3.0
butyl methyl ether (1) +						
C_7H_{16} (2)	1257	23	−33	65	117	2.1
C_6H_{12} (2)	1446	−218	−40	−150		0.7
butyl ethyl ether (1) +						
C_7H_{16} (2)	828	8	91	−33		1.9
C_6H_{12} (2)	988	−249	47	27	84	0.6
dipropyl ether (1) +						
C_7H_{16} (2)	825	−31	13	61		1.3
C_6H_{12} (2)	1015	−258	108			2.2
dibutyl ether (1) +						
C_7H_{16} (2)	403	−51	−49	−2	100	0.7
C_6H_{12} (2)	878	−289	84	83		1.1
dipentyl ether (1) +						
C_7H_{16} (2)	238	−39	6			0.3
C_6H_{12} (2)	775	−242	76	−56		1.9

Table V. Values for the Coefficients a_i, Eq 1, and the Standard Deviations $\sigma(H^E)$, Eq 2, for the Binary Systems Acetals (1) with Heptane (2) or Cyclohexane (2) at 298.15 K

acetal	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$/ J mol^{-1}
2,4-dioxapentane (1) +						
C_7H_{16} (2)	3921	910	−108	50	441	0.8
C_6H_{12} (2)	4067	929	−40	−11	185	1.7
3,5-dioxaheptane (1) +						
C_7H_{16} (2)	2437	139	−75	35	266	0.7
C_6H_{12} (2)	2589	152	−3	88	152	2.4

Table VI. Values for the Coefficients a_i, Eq 1, and the Standard Deviations $\sigma(H^E)$, Eq 2, for the Binary Systems Polyethers (1) with Heptane (2) or Cyclohexane (2) at 298.15 K

polyether	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$/ J mol^{-1}
2,5-dioxahexane (1)						
C_7H_{16} (2)	5210	723	184	−442	−146	0.7
C_6H_{12} (2)	5420	722	−8	−237	346	1.3
3,6-dioxaoctane (1) +						
C_7H_{16} (2)	3501	−102	−122	168	77	0.4
C_6H_{12} (2)	3624	−51	242	131	−446	2.0
2,5,8-trioxanonane (1) +						
C_7H_{16} (2)	6487	−373	−39	308	519	0.5
C_6H_{12} (2)	6632	−681	38	603		1.1
3,6,9-trioxaundecane (1) +						
C_7H_{16} (2)	4771	−722	−23	142	130	0.2
C_6H_{12} (2)	4899	−652	59	−233		0.6
2,5,8,11-tetraoxadodecane (1) +						
C_7H_{16} (2)	6818	−1098	317	−328	−449	0.5
C_6H_{12} (2)	7018	−1164	294	−172	−298	0.5

$H^E_{exptl}(x_1=0.5)$ is ca. 270 J mol^{-1} (13%) smaller than the calculated value.

The $C_{ae,2}$(adj) values, adjusted to the $H^E_{exptl}(x_1=0.5)$'s, are larger (up to 33.5) than $C_{ae,2}$(av) for diethyl ether and for the monoethers containing the methoxy group. On the contrary, $C_{ae,2}$(adj) of symmetrical dialkyl ethers decreases with increasing the chain length of the alkyl group: 26.2 for propyl, 18.5 for butyl, and 14.7 for pentyl. Similar changes have been observed with other homologous series of compounds, e.g., tertiary amines (*25*), and can be attributed to the steric hindrance of the adjacent alkyl groups.

(b) Mixtures of Linear Acetals with n-Alkanes. The proximity of the oxygen atoms in the acetalic group –O–CH_2–O– results in a substantial decrease of the interchange coefficient. The H^E_{exptl} curves of the two investigated acetals (Table II) are reproduced accurately by using $C_{ae,2}$ = 17.5, which is fairly close to the previously reported value, 18.5 (*9*)

$$h_{12}/RT = 17.5\alpha_{1e}^2 \quad \text{(acetals + } n\text{-alkanes)} \qquad (8)$$

(c) Mixtures of Linear Mono- or Polyethers or Acetals with Cyclohexane. H^E of cyclohexane + n-alkanes is relatively small, but nonnegligible. For example, with heptane, $H^E_{exptl}(x_1=0.5$, 298.15 K) = 240 J mol^{-1} (*26*). The interchange enthalpy, $C_{ac,2}$(adj) increases with the chain length of the n-alkane from $C_{ac,2}$(adj) = 0.12 for pentane and hexane, to 0.16 for dodecane, and up to 0.20 for hexadecane. This increase may be attributed to the destruction of orientational order in long-chain n-alkanes during the process of mixing with a globular molecule such as cyclohexane (*27*).

The alkyl segments in the investigated ethers being short (from one C atom, in methyl or methylene, up to five C atoms, in pentyl), the contribution of the a,c contact to H^E should be represented by the lower limit of the interchange coefficient, say, $C_{ac,2}$ = 0.12. Using this value and assuming that $C_{ce,2}$ = $C_{ae,2}$ (29.0 for mono- or polyethers and 17.5 for acetals)

$$h_{12}/RT = 29.0\alpha_{1e}^2 - 0.12\alpha_{1e} + 0.12 \quad \text{(mono-or polyethers + cyclohexane)} \qquad (9)$$

$$h_{12}/RT = 17.5\alpha_{1e}^2 - 0.12\alpha_{1e} + 0.12 \quad \text{(acetals + cyclohexane)} \qquad (10)$$

we calculate $H^E(x_1=0.5)$'s which differ from $H^E_{exptl}(x_1=0.5)$ by less than 150 J mol^{-1}. The largest discrepancies are noted for the same sterically hindered ethers as in mixtures with n-alkanes.

Equation 3 reproduces fairly well the composition dependence of H^E. However, a careful examination reveals that the H^E curves are somewhat broader and flatter than the calculated ones, indicating that the mixtures are not entirely random. This is supported by recent excess heat capacity measurements (*11–13*, *28*) showing that the effect accentuates with decreasing the temperature, especially in the case of tri- and tetraethers. Moreover, polyethers containing three or more oxyethylene groups are not completely miscible (or show microphase separation phenomena) in mixture with long-chain alkanes at or slightly below room temperture (*29*). The discrepancy between H^E calculated and H^E_{exptl}, observed in the case of 2,5,8,11-tetraoxadodecane + heptane (see above), may be due to either incomplete mixing of the components or persistence of an organized structure in the liquid phase. This is corroborated by other H^E measurements, where the observed discrepancies are even larger (Benson, G. C., private communication, 1986).

A detailed interpretation of these results in terms of DISQUAC, an extended quasi-chemical group contribution model (*2*), will be presented separately.

Glossary

a_i	coefficients of eq 1
G	molar Gibbs energy, J mol^{-1}
H	molar enthalpy, J mol^{-1}
T	temperature, K
α	molecular surface fraction

Superscript

E	excess property

Subscripts

i	type of molecule (component)
exptl	experimental
a, b, e	type of contact surface: a, CH_3, CH_2; b, cyclohexane; e, oxygen
s, t	contact surfaces

Registry No. Heptane, 142-82-5; cyclohexane, 110-82-7; diethyl ether, 60-29-7; butyl methyl ether, 628-28-4; butyl ethyl ether, 628-81-9; dipropyl

ether, 111-43-3; dibutyl ether, 142-96-1; dipentyl ether, 693-65-2; 2,4-dioxapentane, 109-87-5; 3,5-dioxaheptane, 462-95-3; 2,5-dioxahexane, 110-71-4; 3,6-dioxaoctane, 629-14-1; 2,5,8-trioxanonane, 111-96-6; 3,6,9-trioxaundecane, 112-36-7; 2,5,8,11-tetraoxadodecane, 112-49-2.

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Infinite Dilution Diffusion Coefficients of Methanol and 2-Propanol in Water

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Infinite dilution diffusion coefficients of methanol and 2-propanol in water have been measured by the Taylor dispersion technique over the temperature range 30–120 °C. Using the data of Pratt and Wakeham and Esteal and Woolf at lower temperatures, we examined the Othmar and Thakar equation (1953) over the entire temperature range. It is found that there are significant deviations above 75 °C.

Introduction

Diffusion coefficients in water are of significance in evaluating theories of diffusion and the liquid state since water/alcohol systems exhibit strong hydrogen bonding. Data in the literature are limited in the temperature range with most measurements being at ambient conditions. The objective of this work was to measure the diffusion coefficients of methanol and 2-propanol in water at a temperature range from 30 to 120 °C. In order to prevent water from boiling, the measurements were made at a pressure of 400 kPa (about 58 psia). Our previous studies indicate that the diffusion coefficients in liquids are independent of pressure in a narrow pressure range of 14.7–500 psia (*1*).

Experimental Technique

Mutual diffusion coefficients of the alcohols were measured by the Taylor dispersion method (*2*). In this method, a narrow pulse of solute diluted in the solvent is injected into a tube in which the solvent is moving in slow laminar flow. The pulse ultimately assumes a Gaussian distribution whose temporal variance is dependent on both the average flow velocity and molecular diffusivity D_{12}. At the end of the diffusion tube the concentration versus time data is recorded as the peak elutes. The normalized first and second temporal moments are calculated from which the diffusion coefficient is obtained. The apparatus and working equations have been described previously (*1*, *3*).

Table I. Infinite Dilution Diffusion Coefficients of Methanol and 2-Propanol in Water

	$D_{12} \times 10^5$, cm^2/s	
T, °C	MeOH	i-PrOH
30	1.83	1.43
56	3.42	2.21
81	4.91	3.32
120	7.73	5.82

Results and Discussion

Measured infinite dilution diffusion coefficients of methanol and 2-propanol in water are given in Table I. A 95% confidence interval of ±5% of the mean is generally sufficient for the data. Previous measurements on diffusion of alcohols in water were performed at temperatures below 65 °C, so this work almost doubles the temperature range of available data. Figure 1 shows data from this work along with those of Pratt and Wakeham (*4*) for 2-propanol in water and those of Esteal and Woolf (*5*) for methanol in water. Pratt and Wakeham also

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