Excess Volumes of Mixtures of Oxolane, Oxane, 1,3-Dioxolane, and 1,4-Dioxane with *n*-Alkanes at 298.15, 308.15, and 318.15 K

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Molar excess volumes V^E have been measured as a function of mole fraction at 298.15, 308.15, and 318.15 K for binary liquid systems of the type cyclic ether (x_1) + *n*-alkane by using pycnometry and, in three cases, vibrating-tube densimetry (VTD). The cyclic ethers were oxolane (tetrahydrofuran, C_4H_8O), oxane (tetrahydropyran, $C_5H_{10}O$), 1,3-dioxolane (1,3-$C_3H_6O_2$), and 1,4-dioxane (1,4-$C_4H_8O_2$); the *n*-alkanes were *n*-decane and *n*-tetradecane. V^E for 1,4-dioxane + *n*-heptane was determined for 298.15 K only. All excess volumes are positive. $V^E(x_1 = 0.5)$ for any mixture containing an m_c-membered cyclic diether is considerably larger than for the corresponding mixture (i.e., with the same *n*-alkane) involving an m_c-membered cyclic monoether. For a given ether, V^E shows a pronounced increase with increasing chain length of the *n*-alkane.

Introduction

Continued interest in the thermodynamics of binary liquid mixtures containing *n*-alkanes makes it desirable to study systematically the influence of chain length *n* of the *n*-alkane *n*-C_nH_{2n+2} *and* of chemical structure of the other component upon excess thermodynamic quantities. Such investigations have recently yielded quite unexpected results (*1*, *2*), which were used subsequently to reexamine and augment existing theories of liquid mixtures. For instance, mixtures of *n*-alkanes with more or less globular molecules, such as tetrachloromethane or cyclohexane, have been discussed by Patterson et al. in terms of destruction of partial order (correlation of molecular motion) assumed to exist in pure liquid *n*-alkanes of sufficient chain length and at temperatures well below the critical (*3*-*9*). Heintz and Lichtenthaler have introduced an extended version of the Flory theory (*10*, *11*), and quite recently Kohler et al. (*12*, *13*) presented a careful study of the volumetric behavior of mixtures of the type cycloalkane + *n*-alkane and its relation to packing effects. Our own activities have focused upon systematic determination of excess enthalpy and excess heat capacity at constant pressure of mixtures of *n*-alkanes with rather large, sterically anisotropic substances of medium polarity, such as halobenzenes (*14*-*17*), 1-chloronaphthalene (*18*), and cycloethers (*19*). For a substantial number of these mixtures molar excess volumes were also determined. However, the cubic coefficient of expansion, though indispensable for the indirect evaluation of either isothermal compressibility or heat capacity at constant volume via ultrasonic speed measurements (see, for example, ref *20* and *21*), has been measured only for a few systems in the series 1,2,4-trichlorobenzene + *n*-alkane (*22*, *23*). As a contribution toward a more comprehensive thermodynamic description along these lines we report here excess volumes of mixtures of oxolane (tetrahydrofuran, C_4H_8O), oxane (tetrahydropyran, $C_5H_{10}O$), 1,3-dioxolane (1,3-$C_3H_6O_2$), and 1,4-dioxane (1,4-$C_4H_8O_2$) each with *n*-decane and *n*-tetradecane at 298.15, 308.15, and 318.15 K. In addition, results on 1,4-dioxane + *n*-heptane at 298.15 K are presented.

Experimental Section

Materials. Oxolane (with purity >99.5 mol %) and 1,4-dioxane (>99.5 mol %) were from C. Erba; oxane (purum, >98 mol %), 1,3-dioxolane (purum, >99 mol %), *n*-heptane (puriss., >99.5 mol %), *n*-decane (purum, >99 mol %), and *n*-tetradecane (puriss., >99 mol %) were from Fluka. The cyclic ethers were fractionally distilled over sodium wire and stored in the dark (*19*), and the *n*-alkanes were used as received. Prior to actual measurement, all liquids were carefully dried with molecular sieve (Union Carbide Type 4A, beads, from Fluka).

Measurements. Densities ρ were measured either pycnometrically or with a vibrating-tube densimeter. The pycnometers were of the single-arm type with volumes of about 20 cm^3 and internal diameters of the capillaries of about 1 mm. They were calibrated at 298.15, 398.15, and 318.15 K with doubly distilled water (*24*) showing a resistivity greater than 10^4 Ω m. The temperature of the thermostat was maintained constant to within ±0.005 K at the desired value and checked by means of a calibrated platinum resistance thermometer. The vibrating-tube densimeter (from Sodev, Model 02D) was operated under flow conditions (*21*, *25*). It was calibrated with distilled water and dry nitrogen at atmospheric pressure. Temperature in that thermostat was maintained constant to within ±0.003 K. Binary mixtures were prepared by mass. The possible error in the mole fractions is estimated to be less than 10^{-4}.

From the densities, the molar excess volumes V^E were obtained according to

$$V^E = V_m - (x_1V_1 + x_2V_2)$$
$$= x_1M_1(\rho_m^{-1} - \rho_1^{-1}) + x_2M_2(\rho_m^{-1} - \rho_2^{-1}) \qquad (1)$$

Here, V_i, M_i, ρ_i, and x_i denote respectively the molar volume, the molar mass, the density, and the mole fraction of either cycloether (i = 1) or *n*-alkane (i = 2); quantities with subscript m refer to the mixture. We estimate the imprecision of the pycnometric V^E to be about ±0.008 cm^3 mol^{-1}, which value is supported (with very few exceptions) by the standard deviations (see below).

Results and Discussion

Densities of the pure liquids are listed in Table I. In general, agreement with literature data (*26*-*35*) is satisfactory. Molar excess volumes as determined via eq 1 are presented in Tables II and III. The latter contains results by vibrating-tube densimetry (VTD), obtained in two separate series of measure-

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Table I. Experimental Densities ρ of Pure Liquids at 298.15, 308.15, and 318.15 K, and Comparison with Selected Literature Data at 298.15 K

liquid	ρ/(kg m^{-3}) exptl at 298.15 K	at 308.15 K	at 318.15 K	lit. at 298.15 K
n-heptane	679.48			679.51 (*26*), 679.43 (*27*)
n-decane	726.72	719.15	711.41	726.25 (*26*), 726.37 (*28*)
n-tetradecane	759.60	752.53	745.52	759.30 (*29*), 759.18 (*28*)
oxolane	882.69	872.02	860.81	882.3 (*30*), 881.97 (*31*)
oxane	879.16	869.13	858.95	879.22,[a] 879.1 (*33*)
1,3-dioxolane	1058.65	1046.20	1033.64	1059.1 (*33*), 1053.8[b]
1,4-dioxane	1027.92	1016.59	1005.26	1027.97 (*26*), 1028.21 (*35*)

[a] Interpolated value from ref *32*. [b] Extrapolated value from ref *34*.

ments several months apart. At each temperature, the excess volumes were fitted with a smoothing polynomial

$$V^E/(\text{cm}^3\ \text{mol}^{-1}) = x_1x_2 \sum_{i=0}^{k-1} A_i(x_1 - x_2)^i \tag{2}$$

by the method of unweighted least squares. The k coefficents A_i and the standard deviations σ are given in Table IV.

For 1,4-dioxane + n-decane, and + n-tetradecane, excess volumes were determined at 298.15 K by pycnometry as well as vibrating-tube densimetry. Agreement between these two techniques is reasonable in both cases as evidenced by Figure 1, though for mixtures rich in 1,4-dioxane (that is to say, for $x_1 > 0.5$) the pycnometric data are slightly smaller than the VTD results.

Excess volumes of 1,4-dioxane + n-heptane were measured by Deshpande and Oswal (DO) (*36*) at 303.15 K. At $x_1 = 0.5$ they reported $V^E = 0.749$ cm^3 mol^{-1}. Adjustment of their data to 298.15 K is possible only by estimating $\partial V^E/\partial T$ through analogy with the temperature dependence of V^E for the systems 1,4-dioxane + n-decane, and 1,4-dioxane + n-tetradecane. At equimolar composition, a reasonable estimate (see below) is $\partial V^E/\partial T = 4.1 \times 10^{-3}$ cm^3 K^{-1} mol^{-1}, which value

Table II. Molar Excess Volumes V^E for Binary Liquid Mixtures of Cyclic Ether (x_1) + n-Alkane (x_2) at 298.15, 308.15, and 318.15 K Obtained via Pycnometry

x_1	V^E/(cm^3 mol^{-1}) at 298.15 K	at 308.15 K	at 318.15 K	x_1	V^E/(cm^3 mol^{-1}) at 298.15 K	at 308.15 K	at 318.15 K
x_1 C_4H_8O + x_2 n-$C_{10}H_{22}$							
0.2384	0.352_4	0.375_1	0.396_3	0.7408	0.473_6	0.505_3	0.534_6
0.3371	0.473_6	0.495_8	0.513_7	0.8147	0.400_6	0.421_1	0.449_6
0.5453	0.560_1	0.587_9	0.615_2	0.8615	0.318_3	0.342_1	0.362_9
0.7017	0.508_6	0.538_2	0.566_2	0.9335	0.170_4	0.190_3	0.196_4
x_1 C_4H_8O + x_2 n-$C_{14}H_{30}$							
0.2454	0.564_8	0.576_3	0.594_1	0.5633	0.730_8	0.749_7	0.782_4
0.3755	0.696_2	0.715_6	0.760_8	0.7155	0.650_6	0.673_8	0.699_1
0.4822	0.740_6	0.760_2	0.791_2	0.8519	0.461_4	0.507_2	0.521_1
x_1 $C_5H_{10}O$ + x_2 n-$C_{10}H_{22}$							
0.2067	0.256_1	0.260_3	0.264_9	0.7624	0.390_8	0.400_9	0.408_1
0.3320	0.377_8	0.381_9	0.387_7	0.8032	0.335_2	0.348_2	0.355_4
0.4909	0.475_7	0.479_1	0.485_3	0.8561	0.260_6	0.271_8	0.283_1
0.6270	0.483_0	0.496_1	0.503_1	0.9059	0.169_0	0.176_3	0.188_4
x_1 $C_5H_{10}O$ + x_2 n-$C_{14}H_{30}$							
0.2291	0.571_8	0.581_4	0.593_3	0.7158	0.649_1	0.655_8	0.661_9
0.3361	0.700_6	0.711_2	0.724_1	0.7631	0.586_6	0.593_3	0.600_1
0.4898	0.776_2	0.790_7	0.806_0	0.8205	0.484_1	0.490_3	0.496_4
0.5859	0.756_1	0.764_8	0.775_3				
x_1 1,3-$C_3H_6O_2$ + x_2 n-$C_{10}H_{22}$							
0.2109	0.747_3	0.791_1	0.827_3	0.7781	0.736_1	0.808_1	0.871_8
0.2816	0.899_8	0.949_2	1.001_8	0.8429	0.568_8	0.619_8	0.666_7
0.4266	1.073_3	1.150_1	1.224_8	0.8822	0.432_9	0.473_1	0.519_6
0.5329	1.087_6	1.160_2	1.253_4	0.9291	0.250_2	0.278_4	0.298_2
0.6532	0.977_7	1.0573	1.151_8				
x_1 1,3-$C_3H_6O_2$ + x_2 n-$C_{14}H_{30}$							
0.2321	0.920_9	0.958_2	0.997_8	0.5766	1.370_4	1.463_9	1.569_2
0.3375	1.212_1	1.265_4	1.318_2	0.6688	1.257_3	1.353_1	1.466_2
0.4381	1.384_2	1.455_2	1.512_1	0.8220	0.891_1	0.972_8	1.051_0
0.5255	1.429_1	1.500_8	1.581_9				
x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{10}H_{22}$							
0.1827	0.710_8	0.763_2	0.811_2	0.6910	0.947_2	1.002_8	1.045_9
0.2844	0.953_7	1.010_2	1.060_3	0.7898	0.751_4	0.789_7	0.827_6
0.4061	1.094_4	1.141_8	1.196_4	0.8893	0.444_2	0.467_7	0.489_0
0.4903	1.124_9	1.177_6	1.237_0	0.9483	0.209_1	0.226_4	0.237_4
0.6229	1.045_1	1.097_0	1.151_6				
x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{14}H_{30}$							
0.1847	0.763_1	0.791_4	0.834_4	0.7851	1.067_3	1.116_0	
0.2777	1.078_7	1.128_9	1.181_6	0.8544	0.830_6	0.872_1	0.922_2
0.4513	1.409_8	1.467_7	1.537_1	0.9232	0.505_1	0.525_3	0.565_9
0.6033	1.403_9	1.457_2	1.554_9	0.9443	0.379_0	0.393_6	0.416_1
0.7249	1.218_3	1.287_0	1.354_8				

Table III. Molar Excess Volumes V^E for Binary Mixtures of 1,4-Dioxane (x_1) + n-Alkane (x_2) at 298.15 K, Obtained via Vibrating-Tube Densimetry

x_1	V^E/(cm³ mol⁻¹)	x_1	V^E/(cm³ mol⁻¹)
x_1 1,4-$C_4H_8O_2$ + x_2 n-C_7H_{16}			
0.0410	0.153_4	0.5335	0.706_7
0.0927	0.315_5	0.5713	0.684_0
0.1374	0.392_2	0.6126	0.653_5
0.1971	0.552_9	0.6753	0.587_7
0.2599	0.637_9	0.7539	0.482_7
0.3368	0.710_1	0.8202	0.378_6
0.3724	0.726_2	0.8361	0.351_8
0.4136	0.733_5	0.9108	0.201_7
0.4761	0.731_9	0.9466	0.126_5
0.5132	0.717_6		
x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{10}H_{22}$			
0.0686	0.297_1	0.5464	1.129_4
0.0789	0.337_6	0.6159	1.083_2
0.1425	0.566_4	0.6731	1.016_0
0.1874	0.701_5	0.7165	0.944_5
0.2659	0.902_5	0.7602	0.856_0
0.2873	0.937_4	0.8072	0.743_3
0.3680	1.070_7	0.8457	0.631_6
0.3897	1.086_9	0.8801	0.519_4
0.4345	1.120_8	0.9111	0.403_3
0.5181	1.145_2	0.9450	0.259_4
0.5290	1.144_7	0.9773	0.104_9
x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{14}H_{30}$			
0.1251	0.567_8	0.8553	0.879_2
0.2247	0.921_4	0.8925	0.712_5
0.3480	1.241_7	0.9062	0.643_6
0.3993	1.334_2	0.9167	0.584_0
0.5481	1.441_9	0.9415	0.443_4
0.6621	1.372_3	0.9617	0.307_8
0.6705	1.360_4	0.9719	0.234_9
0.8206	1.002_6	0.9747	0.211_7

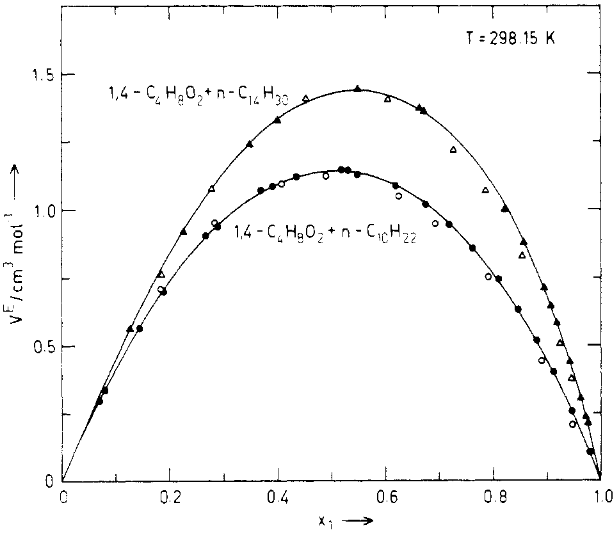

Figure 1. Molar excess volumes V^E of binary liquid mixtures of 1,4-dioxane + n-decane (○, ●) and 1,4-dioxane + n-tetradecane (△, ▲) at 298.15 K, plotted against mole fraction x_1 of the cyclic ether. Open symbols denote experimental results obtained pycnometrically; filled symbols are results obtained by vibrating-tube densimetry. Curves correspond to least-squares representations of VTD data by eq 2 with parameters from Table IV.

Table IV. Coeffcients A_i and Standard Deviations $\sigma(V^E)$ for Representation of Molar Excess Volumes at 298.15, 308.15, and 318.15 K by Eq 2

	T/K	A_0	A_1	A_2	A_3	$\sigma(V^E)$/(cm³ mol⁻¹)
	x_1 C_4H_8O + x_2 n-$C_{10}H_{22}$					
	298.15	2.220	0.510	0.134		0.008
	308.15	2.324	0.546	0.266		0.006
	318.15	2.428	0.596	0.339		0.005
	x_1 C_4H_8O + x_2 n-$C_{14}H_{30}$					
	298.15	2.955	0.075	0.840	0.664	0.003
	308.15	3.028	−0.006	0.998	1.406	0.005
	318.15	3.153	0.039	0.938	1.350	0.006
	x_1 $C_5H_{10}O$ + x_2 n-$C_{10}H_{22}$					
	298.15	1.922	0.682	−0.203	−0.587	0.003
	308.15	1.945	0.751	−0.120	−0.670	0.004
	318.15	1.969	0.723	−0.073	−0.507	0.004
	x_1 $C_5H_{10}O$ + x_2 n-$C_{14}H_{30}$					
	298.15	3.102	0.011	0.458		0.002
	308.15	3.149	−0.006	0.454		0.003
	318.15	3.201	−0.035	0.451		0.004
	x_1 1,3-$C_3H_6O_2$ + x_2 n-$C_{10}H_{22}$					
	298.15	4.383	−0.198	−0.098		0.011
	308.15	4.692	−0.080	−0.069		0.011
	318.15	5.050	0.079	−0.244		0.013
	x_1 1,3-$C_3H_6O_2$ + x_2 n-$C_{14}H_{30}$					
	298.15	5.642	0.125	−0.470	2.012	0.017
	308.15	5.952	0.425	−0.280	1.943	0.012
	318.15	6.272	1.228			0.011
	x_1 1,4-$C_4H_8O_2$ + x_2 n-C_7H_{16}					
VTD[a]	298.15	2.898	−0.707	0.266		0.008
	x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{10}H_{22}$					
	298.15	4.496	−0.239	0.320		0.008
	308.15	4.700	−0.185	0.591	−0.352	0.007
	318.15	4.924	−0.206	0.692	−0.468	0.007
VTD[a]	298.15	4.567	0.109	0.343		0.006
	x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{14}H_{30}$					
	298.15	5.741	0.528	0.046	1.458	0.002
	308.15	5.982	0.616	0.106	1.414	0.007
	318.15	6.299	0.784	0.188	1.298	0.006
VTD[a]	298.15	5.705	0.868	0.895	1.051	0.008

[a] VTD signifies vibrating-tube densimetry.

Table V. Interpolated Values of $\partial V^E/\partial T$ at $x_1 = 0.5$, Evaluated over the Experimental Temperature Range

system	$10^3 \times [\partial V^E(x_1 = 0.5)/\partial T]$/(cm³ K⁻¹ mol⁻¹)
x_1 C_4H_8O + x_2 n-$C_{10}H_{22}$	2.6
+ x_2 n-$C_{14}H_{30}$	2.5
x_1 $C_5H_{10}O$ + x_2 n-$C_{10}H_{22}$	0.6
+ x_2 n-$C_{14}H_{30}$	1.2
x_1 1,3-$C_3H_6O_2$ + x_2 n-$C_{10}H_{22}$	8.3
+ x_2 n-$C_{14}H_{30}$	7.9
x_1 1,4-$C_4H_8O_2$ + x_2 n-$C_{10}H_{22}$	5.4
+ x_2 n-$C_{14}H_{30}$	7.0

yields V^E(DO, 298.15 K) = 0.728 cm³ mol⁻¹, in good agreement with our result V^E = 0.725 cm³ mol⁻¹. No other results could be found for comparison.

At x_1 = 0.5, V^E is considerably larger for any mixture of an m_c-membered cyclic diether (m_c = 5 or 6) with an n-alkane than for the corresponding mixture involving an m_c-membered cyclic monoether, whereas the ring size itself influences V^E only weakly. For instance, at 298.15 K $V^E(x_1 = 0.5)$ = 1.410 cm³ mol⁻¹ for 1,3-$C_3H_6O_2$ + n-$C_{14}H_{30}$ (m_c = 5) as compared to $V^E(x_1 = 0.5)$ = 0.737 cm³ mol⁻¹ for C_4H_8O + n-$C_{14}H_{30}$ (m_c = 5), and $V^E(x_1 = 0.5)$ = 0.754 cm³ mol⁻¹ for $C_5H_{10}O$ + n-$C_{14}H_{30}$ (m_c = 6). For any given ether, V^E shows a pronounced increase with increasing n as observed with other cyclic compounds in ref *13*, *17*, and *18*.

Table V contains (interpolated) values of $\partial V^E/\partial T$ for x_1 = 0.5, evaluated over the experimental temperature range through linear smoothing of the respective Redlich–Kister coefficients A_0 of Table IV. We note that (a) $\partial V^E/\partial T$ is larger for any mixture containing an m_c-membered cyclic diether as compared to the corresponding mixture of an m_c-membered cyclic monoether with the same *n*-alkane and (b) $\partial V^E/\partial T$ increases with increasing chain length of the *n*-alkane for the series with six-membered cyclic ethers, whereas for the series containing five-membered cyclic ethers $\partial V^E/\partial T$ decreases slightly with increasing *n*.

A detailed discussion of all our results on mixtures of cycloethers with *n*-alkanes, including data reported in ref *19*, is deferred until heat capacities and ultrasonic speeds are available.

Registry No. Oxolane, 109-99-9; oxane, 142-68-7; 1,3-dioxolane, 646-06-0; 1,4-dioxane, 123-91-1; *n*-heptane, 142-82-5; *n*-decane, 124-18-5; *n*-tetradecane, 629-59-4.

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Electrical Conductivity of Concentrated Lithium Bromide Aqueous Solutions

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The electrical conductivity of aqueous lithium bromide solutions was measured at the concentrations of 40-63 wt % of LiBr (6.5-13 M) and temperatures of 15-80 °C. The results are reproducible to within ±0.4-1.5% (3 mmho) and are suitable for analytical determination of LiBr. The absolute accuracy of analytical determination using this method is ±0.3% LiBr in concentrations greater than 50% and ±0.7% in concentrations of 40-50% LiBr. Data compare favorably with previous publications.

Concentrated lithium bromide solutions are used in absorption air conditioning machines. These are used as central units to control the temperature and humidity in buildings where there is waste steam, or in places where the vibrations created by centrifugal central air conditioners are unacceptable (*1*, *2*). Absorption air conditioners are also important in solar energy utilization (*3*). Thus, the determination of LiBr in concentrated solution is of practical value.

There are two known methods for the determination of LiBr: by titration with $AgNO_3$ (*4*) and by measurement of the density of the solution (*5*). Both methods give accurate results and correspond to each other (*6*). However, another analytical method may be derived, one that does not require expensive reagents, skilled technical personnel, or large volumes of sample. Such a method could be measurement of conductivity of the LiBr solution. Moreover, conductivity values could be measured inside the machine, without having to extract samples.

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