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Thermodynamic Properties of Binary Mixtures Containing 1,2-Epoxybutane + Four Alkanols at 298.15 K

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Isothermal vapor−liquid equilibria, VLE, excess molar enthalpies, H_m^E, and excess molar volumes, V_m^E, were determined for 1,2-epoxybutane +methanol, +ethanol, + 1-propanol, and +2-propanol at 298.15 K. The VLE results were correlated with the Wilson equation, and H_m^E and V_m^E were correlated with the Redlich−Kister equation. Nonideality of the vapor phase was accounted for in the analysis of VLE data. Azeotropes occurred in the system 1,2-epoxybutane + methanol and, to a lesser extent, for 1,2-epoxybutane + ethanol.

Introduction

The thermodynamic properties of binary mixtures, such as excess Gibbs free energy, G_m^E, excess molar enthalpy, H_m^E, and excess molar volume, V_m^E, are useful in the study of molecular interactions. Alkanols are protic, associated solvents and when mixed with nonpolar solvents too exhibit large deviations from ideal behavior. This paper reports measurements of VLE, H_m^E, and V_m^E on mixtures of 1,2-epoxybutane, a cyclic ether, with four alkanols. These measurements were made to provide an insight into the extent of deviation from ideality and to analyze the influence of the hydrocarbon chain of the alkanol and the chemical structure of the cyclic ether upon the excess properties. Experimental data for the mixtures mentioned have not been published previously, to our knowledge.

Experimental Section

Materials. Table 1 gives the source and the purities of the materials as received, while Table 2 reports measured densities, ρ, refractive indices, n_D, and boiling points, T_b, and a comparison with literature values. Deviations from literature values never exceed 0.08%.

The 1,2-epoxybutane was distilled with sodium in a Vigreux column, and the first and last 20% of each distillation batch was discarded (after purification, GLC purity was ascertained >99.8 mol %). The other liquids were used as received. All chemicals were degassed just prior to use by placing the unopened containers in an ultrasonic bath. All components were stored in dark bottles over molecular sieves (Union Carbide, type 4A, 1/16 in. pellets) with the exception of ethanol originally supplied with sieves.

Apparatus and Procedure. Isothermal VLE measurements were determined by means of a dynamic glass-recirculating still (Fritz Gmbh, Normag, Hofheim, Germany) described previously by other authors (Gmehling et al., 1980). Temperature and pressure were measured by digital electronic instruments (Normag) with accuracies of ±0.05 K and ±0.05 kPa, respectively. For each data point, ≈30 min elapsed before equilibrium was attained and samples were taken out by syringes. Compositions were determined from density using an Anton Paar digital density meter (model 60) equipped with a density-measuring cell (type 602) with a precision on the measured period τ of 1×10^{-6} s. The density measurements were carried out at (298.15 ± 0.01) K and measured with a digital thermometer (Anton Paar DT-25). The accuracy in density at this temperature is of the order of 5×10^{-5} g·cm^{-3}.

Table 1. Origin and Stated Purity of the Chemicals

component	origin	stated purity/mol %
1,2-epoxybutane	Aldrich Chemical Co.	99 (GC) ap >99.8 (GLC)
methanol	Aldrich Chemical Co.	99.9 (HPLC)
ethanol	Fluka Chemie AG, CH	>99.8 (GC)
1-propanol	Aldrich Chemical Co.	99.5 (ACS)
2-propanol	E. Merck AB, D	99.7 (PA)

The apparatus was calibrated by using dry air and doubly distilled water, and calibration curves were obtained by measuring the density of solutions of ether + alkanol mixtures prepared by mass.

After at least three replicate measurements, the standard deviation on the composition was usually less than 0.001 in mole fraction.

Before measurements, the apparatus was checked with the test mixture benzene + cyclohexane (Wilhelm, 1985). Our V_m^E results are in agreement with literature data of less than 0.5% over the central range of the mole fraction of benzene. This apparatus has also been used to determine densities necessary to estimate excess molar volumes, V_m^E. In this case, solutions were prepared by mass using a Mettler balance (model AE 160) with a precision of 1×10^{-4} g. Precaution were taken to prevent evaporation, and the same procedure was followed as indicated by other authors (Fermeglia and Lapasin, 1988). The nominal mass of the mixtures prepared was ≈15 g, and to minimize the errors in composition, the heavier component was charged first. The densities, ρ, of mixtures were used to calculate the excess molar volumes, V_m^E, according to

$$V_m^E = (x_1M_1 + x_2M_2)/\rho - x_1M_1/\rho_1 - x_2M_2/\rho_2 \qquad (1)$$

where x_i, M_i, and ρ_i are the mole fraction, molar mass, and density of component i, respectively.

The estimated uncertainty in V_m^E was less than 0.001 cm^3 mol^{-1}. Corrections for buoyancy and evaporation of the components were made.

The excess molar enthalpies, H_m^E, were measured in an LKB flow microcalorimeter (model 2107) at $T = 298.15$ K,

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Table 2. Comparison of Densities ρ, Refractive Indices n_D, and Normal Boiling Points T_b of Components with Literature Values

	ρ(298.15 K)/g·cm^{-3}		n_D(298.15 K)		T_b/kPa	
component	exptl	lit.	exptl	lit.	exptl	lit.
1,2-epoxybutane	0.824 63	0.824[a]	1.3815	1.381[a]	336.65	336.574[a]
methanol	0.786 53	0.786 37[a] 0.786 7[b]	1.3264	1.326 52[a]	337.70	337.696[a]
ethanol	0.785 26	0.784 93[a] 0.785 1[b] 0.785 4[c]	1.3593	1.359 41[a]	351.40	351.44[a]
1-propanol	0.799 55	0.799 60[a]	1.3838	1.383 70[a]	370.25	370.301[a]
2-propanol	0.780 87	0.781 26[a] 0.780 86[d]	1.3750	1.375 2[a]	355.40	355.392[a]

[a] Riddick et al., 1986. [b] Papaioannou and Panayiotou, 1995. [c] Nikam et al., 1995. [d] Hiaki et al. 1995.

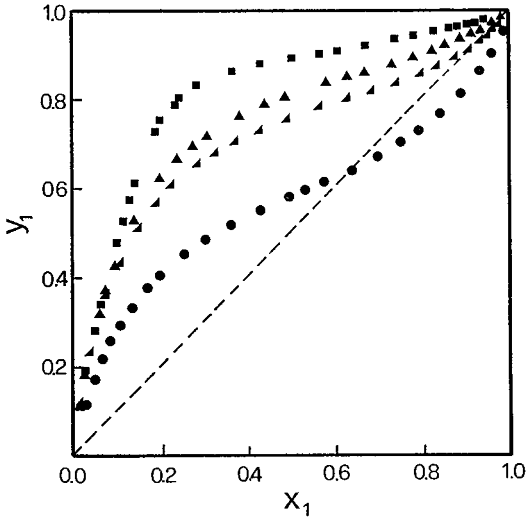

Figure 1. x_1−y_1 plots for 1,2-epoxybutane + alkanols. ●, ◪, ▲, and ■ refer to 1,2-epoxybutane + methanol, +ethanol, +2-propanol, and +1-propanol, respectively.

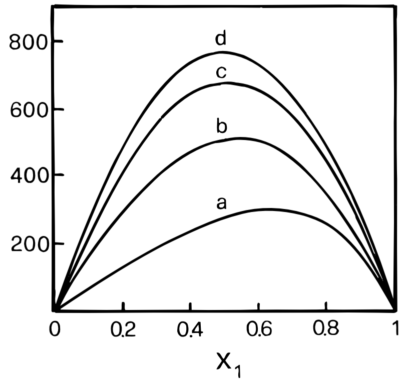

Figure 2. Experimental excess Gibbs free energies, G^E_m, for 1,2-epoxybutane + alkanols. (a−d) refer to 1,2-epoxybutane + 1-propanol, +2-propanol, +ethanol, and +methanol, respectively.

Table 3. Clausius−Clapeyron Coefficients A and B, Eq 2, Correlation Coefficients $|R|$, and Standard Deviations $\sigma(P_i^\circ)$ for the Vapor Pressure P_i° of Pure Components

component	temp range/K	A	B	$\|R\|$	$\sigma(P_i^\circ)$/kPa
1,2-epoxybutane	288−323	7.048 61	−1693.34	0.999 98	0.11
methanol	287−332	7.902 96	−1990.11	0.999 99	0.16
ethanol	287−335	8.318 41	−2213.39	0.999 97	0.18
1-propanol	288−339	8.641 76	−2443.03	0.999 97	0.13
2-propanol	286−334	8.676 19	−2360.46	0.999 96	0.19

maintained constant to within ±0.01 K. Details of the apparatus and its operating procedure were described by Monk and Wadso (1968) and Francesconi and Comelli (1986). Over most of the mole fraction range, the error in H^E_m and in the mole fraction x_1 of 1,2-epoxybutane are estimated to be less than 0.5% and 5×10^{-4}, respectively.

The performance of the calorimeter was checked by measuring H^E_m of the test mixture hexane + cyclohexane at 298.15 K, for which literature values are known (Gmehling, 1993). The agreement was better than 0.5% over the total range of composition.

Results and Discussion

Vapor pressures, P_i°, obtained with the same still used for VLE data, were fitted to the Clausius−Clapeyron equation

$$\log(P_i^\circ/\text{kPa}) = A + B/(T/\text{K}) \qquad (2)$$

The parameters A and B, the correlation coefficients R, and the standard deviation $\sigma(P_i^\circ)$ are reported in Table 3.

The VLE results are listed in Table 4. The x_1 vs y_1 plots at 298.15 K and the excess Gibbs energy G^E_m, are graphically represented in Figures 1 and 2, respectively.

The fugacity coefficients were calculated on the basis of the virial equation of state with the virial coefficients proposed by Prausnitz (1969) and following the procedure described in a previous paper (Francesconi and Cojutti, 1972). Thus, the experimental liquid phase activity coefficients γ_i were obtained from the formula

$$\gamma_i = Py_i/x_iP_i \qquad (3)$$

where P_i is the product of P_i° and a fugacity factor (Van Ness, 1995).

The thermodynamic consistency of the experimental VLE data was checked by means of the modified area test (Francesconi et al., 1996) according to which the integral I

$$I = \int_0^1 [\ln(\gamma_1/\gamma_2) + (V^E_m/RT)\ \mathrm{d}P/\mathrm{d}x_1]\ \mathrm{d}x_1 \qquad (3a)$$

is compared with its uncertainty δI. Thermodynamic consistency of VLE is assumed when $|I|$ and δI are of the same order or $\delta I \geq |I|$.

In our cases, this criterion is satisfied for all four mixtures. Values of $|I|$ and its uncertainty δI are reported in Table 4.

The excess molar Gibbs free energies, G^E_m, Figure 2, were obtained from

$$G^E_m = RT(x_1 \ln \gamma_1 + x_2 \ln \gamma_2) \qquad (4)$$

Table 4. Pressures P, Mole Fractions x_1 and y_1, Experimental Activity Coefficients γ_i, Wilson Parameters a_{12} and a_{21}, Standard Deviation σ from Least-Squares Analysis and Area Test Integral $|I|$ and Its Uncertainty δI for 1,2-Epoxybutane (1) + Alkanols (2) at 298.15 K

P/kPa	x_1	y_1	γ_1	γ_2	P/kPa	x_1	y_2	γ_1	γ_2
1,2-Epoxybutane (1) + Methanol (2)									
18.70	0.027	0.114	3.38	1.01	27.70	0.496	0.583	1.39	1.35
19.65	0.047	0.172	3.08	1.01	27.80	0.529	0.596	1.34	1.40
20.50	0.066	0.215	2.86	1.02	27.90	0.571	0.614	1.28	1.48
21.25	0.087	0.255	2.67	1.02	27.95	0.638	0.642	1.20	1.63
21.90	0.106	0.292	2.58	1.02	27.95	0.697	0.670	1.15	1.79
22.70	0.132	0.333	2.45	1.03	27.75	0.748	0.703	1.11	1.93
23.70	0.169	0.378	2.27	1.05	27.60	0.791	0.733	1.09	2.08
24.30	0.193	0.402	2.16	1.06	27.30	0.840	0.766	1.06	2.35
25.40	0.249	0.451	1.96	1.09	26.70	0.890	0.812	1.04	2.69
26.10	0.299	0.484	1.80	1.13	25.85	0.931	0.870	1.03	2.87
26.75	0.361	0.517	1.63	1.19	25.05	0.958	0.905	1.01	3.34
27.30	0.428	0.551	1.50	1.26	24.30	0.983	0.950	1.00	4.21
$a_{12} = -363.6$; $a_{21} = 4074.8$; $\sigma = 0.048$; $\lvert I\rvert = 0.0029$; $\delta I = 0.038$									
1,2-Epoxybutane (1) + Ethanol (2)									
8.75	0.017	0.120	2.66	1.00	22.20	0.630	0.800	1.21	1.52
9.95	0.039	0.233	2.56	1.01	22.60	0.681	0.819	1.16	1.62
11.55	0.074	0.365	2.45	1.01	22.90	0.737	0.839	1.11	1.78
12.70	0.103	0.436	2.31	1.02	23.20	0.794	0.860	1.07	2.00
14.40	0.149	0.515	2.14	1.04	23.40	0.836	0.879	1.05	2.19
15.60	0.186	0.572	2.05	1.04	23.60	0.873	0.899	1.04	2.38
16.45	0.223	0.615	1.94	1.03	23.80	0.905	0.918	1.03	2.60
17.75	0.278	0.653	1.78	1.08	23.85	0.933	0.936	1.02	2.88
18.50	0.325	0.679	1.66	1.12	23.85	0.950	0.951	1.02	2.96
19.30	0.373	0.708	1.57	1.14	23.80	0.962	0.963	1.02	2.93
20.10	0.428	0.733	1.47	1.19	23.70	0.974	0.972	1.01	3.23
20.90	0.491	0.756	1.38	1.27	23.60	0.981	0.980	1.01	3.14
21.70	0.568	0.782	1.28	1.39					
$a_{12} = 67.4$; $a_{21} = 3171.3$; $\sigma = 0.018$; $\lvert I\rvert = 0.0088$; $\delta I = 0.039$									
1,2-Epoxybutane (1) + 1-Propanol (2)									
3.50	0.015	0.094	0.95	1.15	15.80	0.428	0.882	1.40	1.15
4.30	0.032	0.190	1.10	1.28	16.90	0.504	0.895	1.29	1.27
5.10	0.050	0.282	1.24	1.37	17.70	0.564	0.906	1.22	1.35
5.60	0.065	0.340	1.26	1.41	18.35	0.607	0.910	1.18	1.49
7.05	0.103	0.482	1.42	1.45	19.20	0.671	0.925	1.13	1.55
7.50	0.114	0.525	1.49	1.43	20.15	0.737	0.936	1.10	1.73
8.05	0.131	0.575	1.52	1.40	20.70	0.782	0.945	1.07	1.84
8.55	0.140	0.615	1.62	1.36	21.30	0.824	0.954	1.06	1.96
10.15	0.186	0.730	1.71	1.20	21.65	0.853	0.965	1.05	1.82
10.40	0.195	0.750	1.72	1.15	21.95	0.880	0.970	1.04	1.94
11.35	0.230	0.789	1.67	1.10	22.30	0.903	0.975	1.03	2.03
11.60	0.237	0.802	1.69	1.07	22.60	0.917	0.979	1.03	2.04
12.60	0.282	0.831	1.60	1.05	22.80	0.939	0.986	1.02	1.84
14.60	0.366	0.861	1.48	1.13					
$a_{12} = -1678.0$; $a_{21} = 4425.3$; $\sigma = 0.26$; $\lvert I\rvert = 0.104$; $\delta I = 0.092$									
1,2-Epoxybutane (1) + 2-Propanol (2)									
6.50	0.017	0.106	1.75	1.03	18.65	0.492	0.808	1.31	1.22
7.05	0.028	0.183	1.99	1.03	19.60	0.577	0.836	1.22	1.31
8.35	0.061	0.323	1.90	1.05	20.20	0.630	0.852	1.17	1.40
9.00	0.076	0.137	1.90	1.06	20.70	0.671	0.861	1.14	1.51
9.65	0.094	0.425	1.88	1.06	21.40	0.729	0.882	1.11	1.61
11.20	0.139	0.529	1.83	1.06	21.80	0.777	0.895	1.07	1.77
12.95	0.196	0.620	1.76	1.06	22.25	0.823	0.915	1.06	1.84
14.10	0.236	0.667	1.71	1.07	22.50	0.856	0.924	1.04	2.05
15.00	0.278	0.695	1.61	1.10	22.70	0.883	0.936	1.03	2.14
15.70	0.309	0.719	1.57	1.10	22.90	0.910	0.947	1.02	2.32
16.85	0.380	0.760	1.44	1.13	23.10	0.930	0.958	1.02	2.39
17.90	0.439	0.791	1.38	1.15	23.30	0.965	0.981	1.01	2.18
$a_{12} = -111.8$; $a_{21} = 2645.9$; $\sigma = 0.059$; $\lvert I\rvert = 0.011$; $\delta I = 0.037$									

with γ_i calculated from the Wilson model (Van Ness and Abbot, 1982)

$$\ln \gamma_k = -\ln(x_k - \Lambda_{kj}x_j) + x_j[\Lambda_{kj}/(x_k + \Lambda_{kj}x_j) - a_{jk}/(x_j + \Lambda_{jk}x_k)] \quad (5)$$

$$\Lambda_{ij} = (V_j/V_i)\exp(-a_{ij}/RT) \qquad k = 1, 2;\ k \neq j$$

through the least-squares procedure used in a previous paper (Francesconi et al., 1993), reporting also the minimized objective function.

Table 5. Experimental Excess Molar Enthalpies H_m^E, Adjustable Parameters a_k, and standard deviations $\sigma(H_m^E)$ for Binary Mixtures Containing 1,2-Epoxybutane + Alkanols at 298.15 K

x_1	H_m^E/J·mol^{-1}	x_1	H_m^E/J·mol^{-1}
1,2-Epoxybutane (1) + Methanol (2)			
0.0374	66	0.4823	796
0.0550	101	0.5829	804
0.0721	150	0.6508	788
0.1344	307	0.7366	694
0.1889	438	0.7885	595
0.2369	537	0.8483	450
0.3178	666	0.9179	244
0.4114	762		
$a_0 = 3210.6$; $a_1 = 576.7$; $a_2 = 845.5$; $a_3 = 0$; $a_4 = -2138.8$; $\sigma(H_m^E)$/J·mol^{-1} = 3.4			
1,2-Epoxybutane (1) + Ethanol (2)			
0.0218	54	0.5017	1102
0.0529	137	0.5730	1133
0.0774	207	0.6681	1101
0.1006	288	0.7285	1037
0.1436	437	0.8010	888
0.1828	553	0.8429	760
0.2512	744	0.8895	579
0.3090	868	0.9415	327
0.4015	1020		
$a_0 = 4414.6$; $a_1 = 1178.5$; $a_2 = 1378.5$; $a_3 = 838.0$; $a_4 = -1803.3$; $\sigma(H_m^E)$/J·mol^{-1} = 4.2			
1,2-Epoxybutane (1) + 1-Propanol (2)			
0.0346	75	0.5632	1302
0.0668	176	0.6321	1271
0.0970	289	0.7205	1155
0.1253	404	0.7746	1059
0.1768	611	0.8376	859
0.2226	775	0.8730	725
0.3005	1013	0.9116	545
0.3641	1145	0.9538	309
0.4621	1273		
$a_0 = 5169.3$; $a_1 = 763.8$; $a_2 = 778.0$; $a_3 = 2061.9$; $a_4 = -1570.1$; $\sigma(H_m^E)$/J·mol^{-1} = 4.3			
1,2-Epoxybutane (1) + 2-Propanol (2)			
0.0354	109	0.5690	1507
0.0683	250	0.6376	1454
0.0991	394	0.7252	1301
0.1279	532	0.7787	1166
0.1803	772	0.8407	946
0.2267	974	0.8756	788
0.3055	1235	0.9135	588
0.3696	1383	0.9548	329
0.4680	1496		
$a_0 = 6049.4$; $a_1 = 467.3$; $a_2 = 824.7$; $a_3 = 2146.8$; $a_4 = -1701.8$; $\sigma(H_m^E)$/J·mol^{-1} = 3.2			

Parameters a_i of the Wilson equation and standard deviations σ are reported in Table 4. We have also used other models, like the ones of NRTL and Redlich−Kister (with more parameters), but the best fits were from the Wilson model.

Tables 5 and 6 list the excess molar enthalpies, H_m^E, and the excess molar volumes, V_m^E, for the four binary mixtures, and the experimental values are graphically represented in Figures 3 and 4. The Redlich−Kister equation

$$Q_m^E = x_1 x_2 \sum_{k\geq 0} a_k (x_1 - x_2)^k \quad (6)$$

where $Q_m^E = H_m^E$/J·mol^{-1} or V_m^E/cm^3·mol^{-1} was fitted to the experimental results by a least-squares method, with all points weighted equally. Values of the adjustable parameters a_k and the standard deviations $\sigma(Q_m^E)$ are also listed in Tables 5 and 6. The values of a_k correspond to the

Table 6. Experimental Excess Molar Volumes V_m^E, Adjustable Parameters a_k, and Standard Deviations (V_m^E) for the Binary Mixtures Containing 1,2-Epoxybutane + Alkanols at 298.15 K

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
1,2-Epoxybutane (1) + Methanol (2)					
0.0802	0.787 26	−0.004	0.3522	0.808 33	−0.091
0.0375	0.789 81	−0.018	0.3863	0.809 70	−0.093
0.0686	0.792 29	−0.031	0.4477	0.811 95	−0.094
0.1320	0.796 80	−0.053	0.5132	0.814 10	−0.092
0.1600	0.798 59	−0.061	0.6173	0.817 04	−0.082
0.2107	0.801 55	−0.072	0.7692	0.820 51	−0.053
0.2463	0.803 43	−0.078	0.8614	0.822 27	−0.030
0.2740	0.804 82	−0.082	0.9250	0.823 38	−0.015
0.3251	0.807 17	−0.089			
$a_0 = -0.3706$; $a_1 = 0.0262$; $a_3 = 0.0888$; $\sigma(V_m^E)$/cm^3·mol^{-1} = 0.000 25					
1,2-Epoxybutane (1) + Ethanol (2)					
0.0164	0.786 20	0.001	0.4756	0.807 35	0.048
0.0802	0.789 70	0.007	0.5440	0.809 84	0.056
0.1417	0.792 88	0.012	0.6071	0.812 05	0.061
0.2453	0.797 85	0.021	0.7318	0.816 18	0.066
0.2764	0.799 25	0.025	0.7328	0.816 21	0.066
0.3313	0.801 63	0.030	0.8170	0.818 88	0.060
0.3500	0.802 40	0.033	0.9055	0.821 66	0.040
0.3954	0.804 25	0.038	0.9700	0.823 68	0.015
0.4492	0.806 37	0.043			
$a_0 = 0.2027$; $a_1 = 0.2330$; $a_3 = 0.1225$; $\sigma(V_m^E)$/cm^3·mol^{-1} = 0.000 46					
1,2-Epoxybutane (1) + 1-Propanol (2)					
0.0233	0.800 17	0.005	0.5047	0.812 26	0.089
0.0531	0.800 96	0.012	0.5417	0.813 15	0.093
0.1063	0.802 35	0.024	0.6093	0.814 76	0.097
0.2250	0.805 33	0.047	0.6550	0.815 87	0.096
0.2754	0.806 66	0.056	0.7615	0.818 44	0.090
0.3307	0.808 03	0.065	0.8436	0.820 49	0.072
0.3751	0.809 12	0.072	0.9393	0.822 97	0.035
0.4197	0.810 21	0.079	0.9699	0.823 80	0.019
0.4581	0.811 13	0.085			
$a_0 = 0.3552$; $a_1 = 0.2091$; $a_2 = 0.1003$; $\sigma(V_m^E)$/cm^3·mol^{-1} = 0.000 40					
1,2-Epoxybutane (1) + 2-Propanol (2)					
0.0173	0.781 52	0.021	0.5078	0.801 38	0.318
0.0650	0.783 31	0.075	0.5578	0.803 55	0.319
0.1316	0.785 92	0.138	0.6196	0.806 24	0.314
0.2329	0.789 97	0.214	0.6664	0.808 31	0.304
0.2650	0.791 26	0.234	0.7636	0.812 73	0.263
0.3403	0.794 36	0.272	0.8644	0.817 57	0.183
0.3778	0.795 92	0.286	0.9182	0.820 28	0.122
0.4056	0.797 08	0.295	0.9767	0.823 36	0.039
0.4678	0.799 67	0.313			
$a_0 = 1.2647$; $a_1 = 0.2440$; $a_2 = 0.2249$; $\sigma(V_m^E)$/cm^3·mol^{-1} = 0.000 72					

minimum of the standard deviation $\sigma(Q_m^E)$ defined as

$$\sigma(Q_m^E) = |\phi/(N - n)|^{0.5} \tag{7}$$

with N = number of experimental points and n = number of adjustable parameters. ϕ is the objective function defined as

$$\phi = \sum_{k\geq 0}^{N} {\eta_k}^2$$

where $\eta = Q_{m,calcd}^E - Q_m^E$, $Q_{m,calcd}^E$ being determined from the right hand side of eq 6.

From Figures 1−4, VLE, calorimetric, and volumetric data constitute a set of measurements in agreement as to the regular increase of these properties in passing from 2-propanol to methanol.

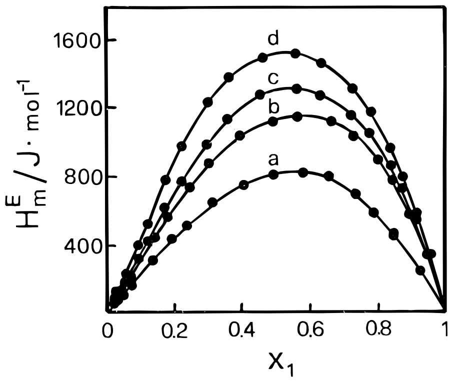

Figure 3. Dependence of the excess molar enthalpy, H_m^E, on the mole fraction x_1 at 298.15 K for binary mixtures containing 1,2-epoxybutane + (a) methanol, +(b) ethanol, +(c) 1-propanol, and +(d) 2-propanol: solid lines, calculated with eq 6.

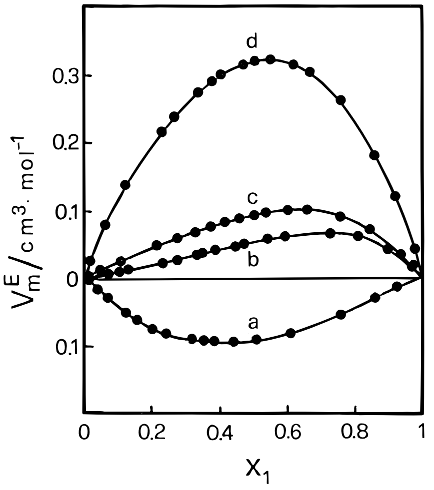

Figure 4. Dependence of the excess molar volume, V_m^E, on the mole fraction x_1 at 298.15 K for binary mixtures containing 1,2-epoxybutane + (a) methanol, +(b) ethanol, +(c) 1-propanol, and +(d) 2-propanol: solid lines, calculated with eq 6.

All alkanols show positive H_m^E values since energy intake for breaking hydrogen bonding prevails over the energy released by interacting dissimilar molecules during mixing. The same results have been obtained from mixtures of alkanols + chloro- or methylcyclohexane (Letcher and Nevines, 1996) and alkanols + cyclic ethers (Letcher and Govender, 1995).

Similarly, V_m^E is positive, except for methanol, due to the increase with the number of molecules when hydrogen bonds are broken. Ortega and Galvan (1995) report V_m^E data showing the same trend as the ones of this paper.

The deviations from ideality, shown in Figure 2, increase from 2-propanol to methanol, in agreement with the increase of association equilibrium constants (Prausnitz, 1969).

Finally, H_m^E's for mixtures of epoxybutane with alkanols are much larger than those for hexane with alkanol (Prausnitz, 1969).

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