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EXCESS PROPERTIES OF MIXTURES OF SOME *n*-ALKOXYETHANOLS WITH ORGANIC SOLVENTS. III. V^E AND C_p^E WITH BUTAN-1-OL AT 298.15 K *

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ABSTRACT

The excess molar volumes, V^E, and the excess molar heat capacities, C_p^E are determined as a function of mole fraction, X, at atmospheric pressure and 298 15 K for 2-methoxyethanol (1), 2-ethoxyethanol (1), 2-butoxyethanol (1), 2-(2-methoxyethoxy)ethanol (1), 2-(2-ethoxyethoxy)ethanol (1), 2-(2-butoxyethoxy)ethanol (1) with butan-1-ol (2) mixtures The V^E values decrease in magnitude as the alkyl chain length of the *n*-alkoxyethanol increases for the two homologous series, they are positive except for the mixtures containing 2-butoxyethanol and 2-(2-butoxyethoxy)ethanol for which they are negative over the whole mole-fraction range The C_p^E values are positive and relatively small for all the mixtures studied

INTRODUCTION

In parts I [1] and II [2] of this series we studied the excess molar functions (H^E, V^E, and C_p^E) of mixtures of an *n*-alkoxyethanol with di-*n*-butylether at 298 15 K and atmospheric pressure In a continuation of these investigations, which concern the study of the excess thermodynamic properties of some mixtures of an *n*-alkoxyethanol with an organic solvent, we report in the present paper the V^E derived from precise density measurements and the C_p^E derived from flow-calorimetric measurements of 2-methoxyethanol (1), 2-ethoxyethanol (1), 2-butoxyethanol (1), 2-(2-methoxyethoxy)ethanol (1), 2,-(2-ethoxyethoxy)ethanol (1), 2-(2-butoxyethoxy)ethanol (1) with butan-1-ol at 298 15 K and atmospheric pressure Excess enthalpies for these mixtures have been reported elsewhere [3,4]

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As far as we know, there have been relatively few thermodynamic studies on such mixtures, except for H^E of butan-1-ol, pentan-1-ol and hexan-1-ol with 2-ethoxyethanol [4], H^E of methanol with 2-ethoxyethanol [5], VLE, H^E and V^E of propan-1-ol with 2-methoxyethanol [6], and H^E and V^E of ethanol with 2-ethoxyethanol [7]

EXPERIMENTAL

Butan-1-ol (Fluka, puriss p a > 99 5 mol%) was used as received The samples of *n*-alkoxyethanols, were the same as those described in [2] Before measurement, the samples were partially degassed and carefully dried over molecular sieves (Union Carbide Type 4A beads from Fluka) Densities and molar heat capacities, at 298 15 K, of the pure liquids were in good agreement with available literature values [2,8]

Binary mixtures were prepared by mass and the error of the final mole fraction is estimated to be less than 0 0001 The excess volumes were calculated from densities measured with a vibrating-tube densimeter from Sodev (Model 02D), operating under flow conditions The excess molar heat capacities were calculated from heat capacities divided by volume (C_p^E/V) measured with a Picker flow microcalorimeter, using the stepwise procedure Details of the experimental techniques have been reported previously [2,8]

RESULTS AND DISCUSSION

The results of measurements of V^E as a function of X at 298 15 K and atmospheric pressure are listed in Table 1 The corresponding C_p^E results are gathered in Table 2 For each mixture, the excess quantities were fitted to a polynomial of the type

$$Q^E = X(1-X)\sum_i A_i(2X-1)^i \qquad (1)$$

by the method of unweighted least squares, where either $Q^E = V^E$ (cm^3 mol^{-1}) or $Q^E = C_p^E$ (J K^{-1} mol^{-1}). The coefficients A_i and the corresponding standard deviations, σ, are given in Table 3 For almost all the mixtures, $\sigma(V^E) < 0\,003$ cm^{-1} mol^{-1} and $\sigma(C_p^E) < 0\,03$ J K^{-1} mol^{-1}, in accord with the imprecision attainable with the instruments used The observed and calculated V^E values [from eqn. (1)] are plotted against X in Fig. 1 and those for C_p^E, in Fig 2 No literature results could be found for comparison.

$V^E(X)$ is negative over the whole mole-fraction range for mixtures containing 2-butoxyethanol and 2-(2-butoxyethoxy)ethanol and positive with the other *n*-alkoxyethanols It decreases as the alkyl chain length of the *n*-alkoxyethanol increases for the two homologous series. This parallels, to

TABLE 1

Excess molar volumes at 298 15 K and atmospheric pressure

X	V^E (cm^3 mol^{-1})	X	V^E (cm^3 mol^{-1})
2-methoxyethanol (1) + butan-1-ol (2)			
0 1116	0 074	0 5956	0 170
0 2148	0 114	0 6934	0 147
0 3039	0 153	0 7861	0 112
0 3955	0 171	0 9075	0 046
0 4939	0 178		
2-ethoxyethanol (1) + butan-1-ol (2)			
0 0709	0 024	0 6035	0 073
0 1189	0 035	0 6927	0 065
0 1955	0 050	0 7923	0 050
0 3291	0 069	0 8864	0 031
0 4125	0 075	0 9367	0 017
0 4935	0 077		
2-butoxyethanol (1) + butan-1-ol (2)			
0 0958	−0 021	0 5981	−0 051
0 1924	−0 037	0 6966	−0 043
0 2937	−0 048	0 7981	−0 034
0 3863	−0 055	0 8842	−0 020
0 4913	−0 060		
2-(2-methoxyethoxy)ethanol (1) + butan-1-ol (2)			
0 0664	0 046	0 4918	0 129
0 1033	0 061	0 5381	0 123
0 1589	0 087	0 5957	0 118
0 2169	0 102	0 6033	0 117
0 2852	0 120	0 7068	0 095
0 2921	0 118	0 7386	0 079
0 3975	0 129	0 8552	0 052
0 4142	0 131	0 8633	0 046
0 4840	0 129	0 9442	0 016
2-(2-ethoxyethoxy)ethanol (1) + butan-1-ol (2)			
0 0626	0 010	0 6205	0 034
0 1734	0 021	0 6974	0 030
0 2949	0 029	0 8405	0 019
0 4143	0 035	0 9129	0 012
0 5033	0 037		
2(2-butoxyethoxy)ethanol (1) + butan-1-ol (2)			
0 1066	−0 045	0 6033	−0 085
0 2066	−0 072	0 7097	−0 067
0 3100	−0 088	0 8151	−0 052
0 4070	−0 094	0 8867	−0 042
0 4939	−0 094		

some extent, the trend for the excess enthalpies, which are less positive for mixtures with longer *n*-alkoxyethanols Values of C_p^E are positive for all the mixtures investigated and are smaller for the series with longer *n*-alkoxyethanols than for the series with shorter *n*-alkoxyethanols

In comparison with the results obtained with di-*n*-butylether [1,2], for a

TABLE 2

Excess molar heat capacities at 298 15 K and atmospheric pressure

X	C_p^E ($J\ K^{-1}\ mol^{-1}$)	X	C_p^E ($J\ K^{-1}\ mol^{-1}$)
2-methoxyethanol (1) + butan-1-ol (2)			
0 1116	1 00	0 5956	1 93
0 2148	1 75	0 6934	1 63
0 3039	2 11	0 7861	1 39
0 3955	2 21	0 9075	0 76
0 4939	2 16		
2-ethoxyethanol (1) + butan-1-ol (2)			
0 0709	0 70	0 6035	1 61
0 1189	1 00	0 6927	1 36
0 1955	1 40	0 7923	0 95
0 3291	1 84	0 8864	0 56
0 4125	1 87	0 9367	0 23
0 4935	1 82		
2-butoxyethanol (1) + butan-1-ol (2)			
0 0958	1 04	0 5981	2 35
0 1924	1 73	0 6966	2 06
0 2937	2 22	0 7981	1 63
0 3863	2 46	0 8842	1 13
2-(2-methoxyethoxy)ethanol (1) + butan-1-ol (2)			
0 0664	0 126	0 5957	0 651
0 1589	0 368	0 7386	0 438
0 2852	0 668	0 8552	0 231
0 3975	0 767	0 9442	0 060
0 4918	0 752		
2-(2-ethoxyethoxy)ethanol (1) + butan-1-ol (2)			
0 0626	0 068	0 5033	0 697
0 1734	0 341	0 6205	0 636
0 2949	0 586	0 8405	0 350
0 4143	0 693	0 9129	0 206
2-(2-butoxyethoxy)ethanol (1) + butan-1-ol (2)			
0 1066	0 54	0 6033	1 34
0 2066	0 95	0 7097	1 14
0 3100	1 27	0 8151	0 86
0 4070	1 41	0 8867	0 66
0 4939	1 43		

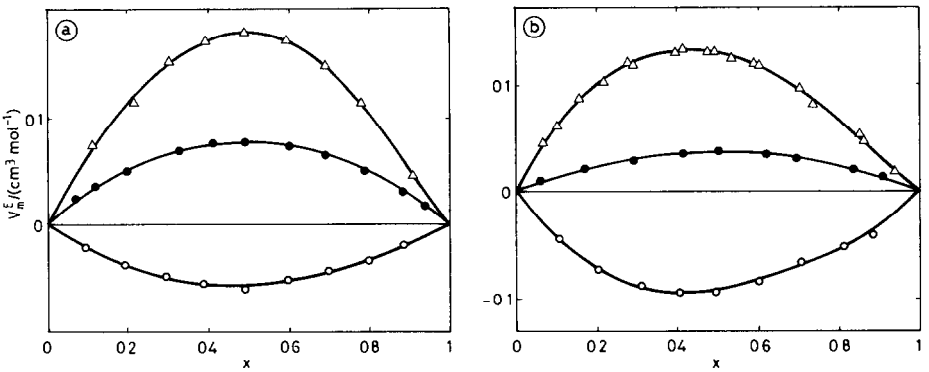

Fig 1 Excess molar volumes V^E for *n*-alkoxyethanol (1) + butan-1-ol (2) mixtures versus X, the mole fraction of component 1 (a) 2-methoxyethanol (△), 2-ethoxyethanol (●), 2-butoxyethanol (○) (b) 2-(2-methoxyethoxy)ethanol (△), 2-(2-ethoxyethoxy)ethanol (●), 2-(2-butoxyethoxy)ethanol (○) Full curves represent the smoothing eqn (1) with the coefficients of Table 3

given *n*-alkoxyethanol, slight differences in V^E are observed when di-*n*-butylether is replaced by butan-1-ol On the other hand, as expected, values of H^E and C_p^E are appreciably more positive in mixtures containing di-*n*-butylether than in mixtures containing butan-1-ol All these factors show the very complex behaviour of these mixtures, where the possible formation of

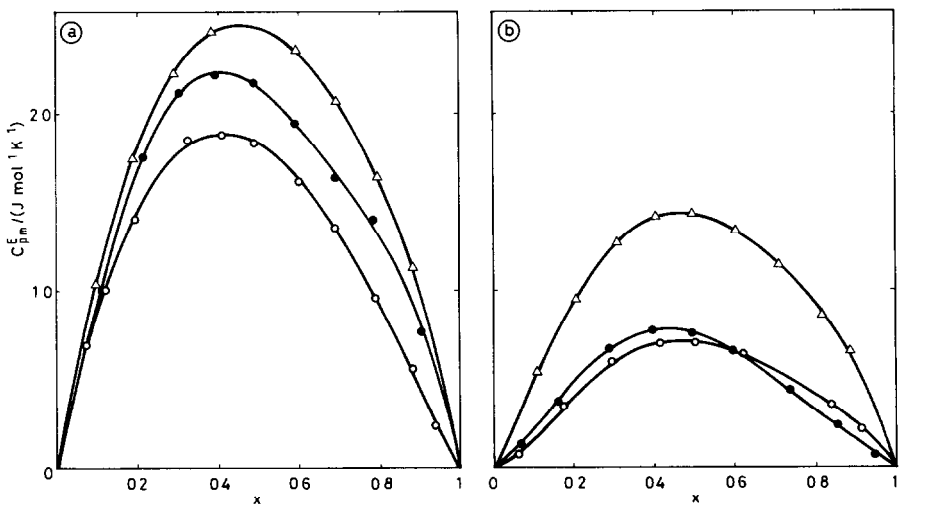

Fig 2 Excess molar heat capacities C_p^E for *n*-alkoxyethanol (1) + butan-1-ol (2) mixtures versus X, the mole fraction of component 1 (a) 2-methoxyethanol (●), 2-ethoxyethanol (○), 2-butoxyethanol (△) (b) 2-(2-methoxyethoxy)ethanol (●), 2-(2-ethoxyethoxy)ethanol (○), 2-(2-butoxyethoxy)ethanol (△) Full curves represent the smoothing eqn (1) with the coefficients of Table 3

TABLE 3

Coefficients A_i and standard deviations $\sigma(Q^E)$ for representation of molar excess quantities at 298 15 K and atmospheric pressure by eqn (1) for *n*-alkoxyethanol (1) + butan-1-ol (2)

n-Alkoxyethanol	A_0	A_1	A_2	A_3	$\sigma(Q^E)$ (J mol^{-1})
$Q^E = V^E$ (cm^3 mol^{-1})					
2-methoxyethanol	0 7153	0 005	−0 106	−0 157	0 003
2-ethoxyethanol	0 3067	−0 004	0 020	−0 034	0 0007
2-butoxyethanol	−0 2267	0 039	0 018	−0 025	0 002
2-(2-methoxyethoxy)ethanol	0 5114	−0 138	0 017	−0 090	0 002
2-(2-ethoxyethoxy)ethanol	0 1438	0 005	0 005	−0 019	0 0009
2-(2-butoxyethoxy)ethanol	−0 3665	0 123	−0 090	−0 132	0 003
$Q^E = C_p^E$ (J K^{-1} mol^{-1})					
2-methoxyethanol	8 567	−3 420	1 77	4 45	0 03
2-ethoxyethanol	7 292	−2 456	0 26	−0 88	0 03
2-butoxyethanol	9 891	−1 342	2 28	1 35	0 02
2-(2-methoxyethoxy)ethanol	3 025	−1 286	−1 52	1 28	0 016
2-(2-ethoxyethoxy)ethanol	2 827	−0 562	−0 93	1 75	0 014
2-(2-butoxyethoxy)ethanol	5 693	−0 821	0 33	2 15	0 02

intramolecular hydrogens bonds in *n*-alkoxyethanols [9–11] must also be considered.

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