Thermochimica Acta, 137 (1989) 241—246
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EXCESS PROPERTIES OF MIXTURES OF SOME n-ALKOXYETHANOLS WITH ORGANIC SOLVENTS.
IV. H^E, V^E AND C_p^E WITH 2-METHOXYETHANOL AT 298.15 K *,**

JOSE CARLOS COBOS, ISAIAS GARCÍA and CARLOS CASANOVA

Departamento de Física Aplicada II, Universidad de Valladolid, 47071 Valladolid (Spain)

GENEVIEVE ROUX-DESGRANGES and JEAN-PIERRE E. GROLIER

Laboratoire de Thermodynamique et Cinetique Chimique, Université Blaise Pascal,
F-63170 Aubière (France)

(Received 12 February 1988)

ABSTRACT

Molar excess enthalpies H^E, molar excess volumes V^E and molar excess heat capacities C_p^E of mixtures of 2-methoxyethanol (1) with 2-ethoxyethanol (2), 2-butoxyethanol (2) and 2-(2-methoxyethoxy)ethanol (2) and H^E of mixtures of 2-methoxyethanol (1) with 2-(2-ethoxyethoxy)ethanol (2) and 2-(2-butoxyethoxy)ethanol (2) were determined as a function of composition at 298.15 K and atmospheric pressure. As expected, owing to the similar chemical nature of the components, the excess functions of these mixtures are relatively small.

INTRODUCTION

As part of our systematic programme of research on the excess thermodynamic properties of some mixtures of n-alkoxyethanols with organic solvents [1–4], we measured the molar excess enthalpies H^E, the molar excess volumes V^E and the molar excess heat capacities C_p^E of mixtures of 2-methoxyethanol (1) with 2-ethoxyethanol (2), 2-butoxyethanol (2) and 2-(2-methoxyethoxy)ethanol (2), and H^E of mixtures of 2-methoxyethanol (1) with 2-(2-ethoxyethoxy)ethanol (2) and 2-(2-butoxyethoxy)ethanol (2) as a function of the mole fraction x of component 1 at 298.15 K and atmospheric pressure.

---

* Communicated in part at the 3rd International Conference on Thermodynamics of Solutions of Non-Electrolytes held in Clermont-Ferrand, France, 1984.
** Part III is ref. 4.

0040-6031/89/$03.50

TABLE 1

Molar excess enthalpy H^E for 2-methoxyethanol + n-alkoxyethanol mixtures at 298.15 K and atmospheric pressure

x	H^E(J mol^{-1})	x	H^E(J mol^{-1})
2-methoxyethanol(1) + 2-ethoxyethanol(2)			
0.0998	13.0	0.5384	39.4
0.1513	18.1	0.5965	38.1
0.1872	22.4	0.6157	37.3
0.2258	26.5	0.6551	36.7
0.2617	29.7	0.6889	34.4
0.2769	30.6	0.7076	33.5
0.3283	34.7	0.7538	30.7
0.3765	36.6	0.7987	26.7
0.4327	38.5	0.8515	21.3
0.4941	39.0	0.8960	16.7
2-methoxyethanol(1) + 2-butoxyethanol(2)			
0.0689	44	0.5245	211
0.1106	68	0.5886	215
0.1487	90	0.6504	207
0.2006	114	0.7010	196
0.2503	139	0.7249	186
0.2887	152	0.7577	179
0.2927	155	0.8110	153
0.3385	175	0.8515	128
0.3758	186	0.9033	89
0.4410	201	0.9415	59
0.4783	209		
2-methoxyethanol(1) + 2-(2-methoxyethoxy)ethanol(2)			
0.1025	−5.9	0.4825	−14.2
0.1513	−6.5	0.5069	−13.5
0.1876	−8.2	0.5835	−12.9
0.2243	−8.5	0.6409	−13.6
0.2422	−8.7	0.6657	−13.3
0.2531	−9.2	0.7191	−11.9
0.2826	−11.5	0.7615	−11.5
0.3327	−12.2	0.8120	−10.5
0.3865	−12.3	0.8503	−8.2
0.4298	−12.2	0.9050	−5.5
0.4440	−12.5	0.9236	−4.2
0.4816	−12.9		
2-methoxyethanol(1) + 2-(2-ethoxyethoxy)ethanol(2)			
0.1692	−4.4	0.5795	−4.7
0.1711	−4.2	0.6041	−5.4
0.1847	−4.5	0.6620	−3.9
0.2510	−5.3	0.7076	−4.5
0.2982	−5.9	0.7538	−2.6
0.3066	−4.9	0.7641	−3.5
0.3475	−5.9	0.8075	−2.0
0.3889	−4.4	0.8561	−3.0

TABLE 1 (continued)

x	H^E(J mol^{-1})	x	H^E(J mol^{-1})
2-methoxyethanol(1) + 2-(2-ethoxyethoxy)ethanol(2)			
0.3916	−4.5	0.8756	−1.3
0.4097	−4.5	0.8798	−1.2
0.4594	−5.6	0.9013	−1.0
0.4986	−5.5	0.9278	−1.2
0.5165	−5.3		
2-methoxyethanol(1) + 2-(2-butoxyethoxy)ethanol(2)			
0.0542	15	0.5452	112
0.1071	29	0.5772	114
0.1423	39	0.5899	113
0.2025	53	0.6303	115
0.2284	60	0.7111	110
0.2848	72	0.7615	101
0.3312	83	0.8098	90
0.3719	90	0.8568	75
0.4188	97	0.9098	54
0.4417	100	0.9511	33
0.4934	106		

EXPERIMENTAL

Materials were the same as used in earlier studies [1–4]. Prior to measurements, all liquids were kept on molecular sieves (Union Carbide type 4A, Fluka) to remove any traces of water, and were partially degassed. Densities and molar heat capacities (at 298.15 K and atmospheric pressure) of the pure liquids agree closely with literature values, as shown in ref. 3.

Binary mixtures were prepared by mass and the error on the final mole fraction was estimated to be less than 0.0001. A standard Calvet microcalorimeter was used to determine the excess enthalpies. The excess volumes were calculated from densities measured with a vibrating-tube densimeter (Sodev Model 02D), operating under flow conditions. The excess molar heat capacities were calculated from heat capacities divided by volume (C_p/V), measured with a Picker flow microcalorimeter using the stepwise procedure. Details of the experimental techniques, auxiliary equipment, calibrations and the accuracy attainable in the values of the excess functions have been described previously [1–5].

RESULTS AND DISCUSSION

The results of our measurements of H^E as a function of x at 298.15 K and atmospheric pressure for the mixtures studied are listed in Table 1. In

TABLE 2

Molar excess volume V^E and molar excess heat capacity C_p^E for 2-methoxyethanol + n-alkoxyethanol mixtures at 298.15 K and atmospheric pressure

x	V^E ($cm^3 mol^{-1}$)	C_p^E ($J mol^{-1} K^{-1}$)	x	V^E ($cm^3 mol^{-1}$)	C_p^E ($J mol^{-1} K^{-1}$)
2-methoxyethanol(1) + 2-ethoxyethanol(2)					
0.1023	0.0053	−0.021	0.5892	0.0085	−0.082
0.2018	0.0076	−0.040	0.6799	0.0071	−0.080
0.2853	0.0079	−0.051	0.7913	0.0054	−0.074
0.4151	0.0092	−0.077	0.8874	0.0029	−0.038
0.4928	0.0085	−0.071			
2-methoxyethanol(1) + 2-butoxyethanol(2)					
0.1202	0.044	−0.031	0.6088	0.126	−0.041
0.2113	0.072	−0.032	0.7131	0.114	−0.059
0.3163	0.097	−0.018	0.8087	0.093	−0.062
0.4103	0.114	−0.031	0.9002	0.059	−0.045
0.5119	0.126	−0.037			
2-methoxyethanol(1) + 2-(2-methoxyethoxy)ethanol(2)					
0.1020	−0.0142	0.059	0.6218	−0.0226	0.140
0.1664	−0.0193	0.109	0.7413	−0.0175	0.115
0.2987	−0.0225	0.137	0.8640	−0.0103	0.082
0.4243	−0.0234	0.162	0.9345	−0.0049	0.040
0.5194	−0.0233	0.149			

TABLE 3

Coefficients A_i in eqn (1) and standard deviations $s(Q^E)$ at 298.15 K and atmospheric pressure for 2-methoxyethanol(1) + n-alkoxyethanol(2) mixtures

2-methoxyethanol	A_0	A_1	A_2	A_3	$s(Q^E)$
$Q^E = H^E$ ($J mol^{-1}$)					
2-ethoxyethanol	157.63	4.08	1.43	29.85	0.3
2-butoxyethanol	841.93	225.57	28.34	−12.28	1.6
2-(2-methoxyethoxy)ethanol	−53.60	−9.66	−11.70		0.6
2-(2-ethoxyethoxy)ethanol	−20.58	9.30	−5.40		0.6
2-(2-butoxyethoxy)ethanol	431.18	203.55	70.40	16.37	0.8
$Q^E = V^E$ ($cm^3 mol^{-1}$)					
2-ethoxyethanol	0.0349	−0.0046	0.0122	−0.021	0.0003
2-butoxyethanol	0.4956	0.1331	0.0502	0.024	0.0011
2-(2-methoxyethoxy)ethanol	−0.0940	0.0069	−0.0424	0.063	0.0004
$Q^E = C_p^E$ ($J mol^{-1} K^{-1}$)					
2-ethoxyethanol	−0.3129	−0.1562	−0.040	0.051	0.006
2-butoxyethanol	−0.1289	−0.1630	−0.435		0.005
2-(2-methoxyethoxy)ethanol	0.6164	−0.1427	0.144	0.196	0.007

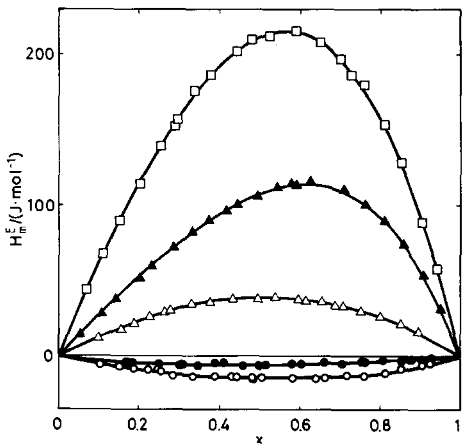

Fig. 1. Molar excess enthalpy H^E for 2-methoxyethanol(1) + n-alkoxyethanol(2) mixtures versus x (the mole fraction of component 1) at 298.15 K and atmospheric pressure: △, 2-ethoxyethanol; □, 2-butoxyethanol; ○, 2-(2-methoxyethoxy)ethanol; ●, 2-(2-ethoxyethoxy) ethanol; ▲, 2-(2-butoxyethoxy)ethanol. Full curves represent the smoothing eqn. (1) with the coefficients of Table 3.

the same way, those for V^E and C_p^E are presented in Table 2. For each mixture, the excess quantities were fitted to a polynomial of the type

$$Q^E = x(1-x)\sum_{i=0}^{k} A_i(2x-1)^i \tag{1}$$

by the method of unweighted least squares, where either $Q^E = H^E(\mathrm{J\ mol^{-1}})$,

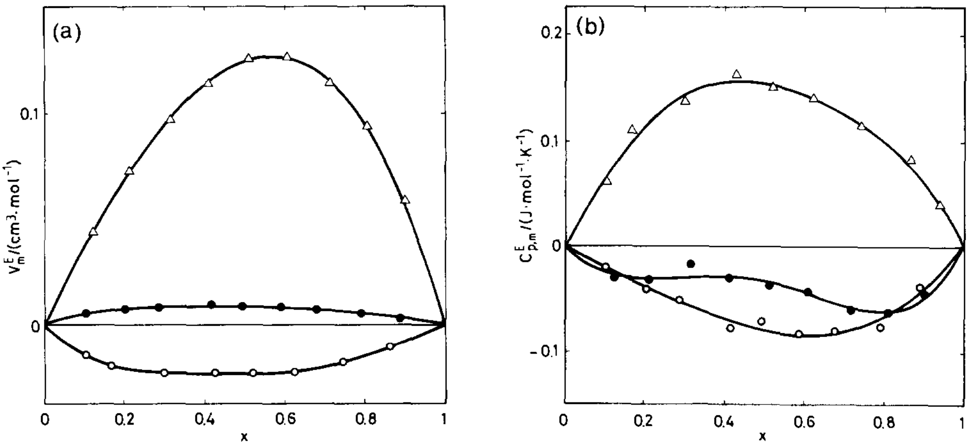

Fig. 2. Molar excess volume V^E and molar excess heat capacity C_p^E for 2-methoxyethanol(1) + n-alkoxyethanol(2) mixtures versus x (the mole fraction of component 1) at 298.15 K and atmospheric pressure. V^E (a): ●, 2-ethoxyethanol; △, 2-butoxyethanol; ○, 2-(2-methoxyethoxy)ethanol. C_p^E (b): ○, 2-ethoxyethanol; ●, 2-butoxyethanol; △, 2-(2-methoxyethoxy)ethanol. Full curves represent the smoothing eqn. (1) with the coefficients of Table 3.

$Q^E = V^E(\text{cm}^3\text{mol}^{-1})$ or $Q^E = C_p^E(\text{J mol}^{-1}\ \text{K}^{-1})$. The coefficients A_i and the corresponding standard deviations $s(Q^E)$ are given in Table 3. For almost all the mixtures $s(H^E) < 1$ J mol^{-1}, $s(V^E) < 0.001$ cm^3 mol^{-1} and $s(C_p^E) <$ 0.007 J mol^{-1} K^{-1}, showing the good accuracy attainable with the instruments used. The observed and calculated H^E values (from eqn. (1)) are plotted against x in Fig. 1. Those for V^E and C_p^E are given in Fig. 2. No results could be found in the literature for comparison.

As expected, owing to the similar chemical nature of the components, the excess molar enthalpies of these mixtures are small. $H^E(x)$ is negative over the entire range of mole fraction for mixtures containing 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol, and is positive with the other n-alkoxyethanols. H^E increases as the alkyl chain length of the n-alkoxyethanol increases for the two homologous series. The H^E values are skewed towards the 2-methoxyethanol-rich side for mixtures with 2-butoxyethanol and 2-(2-butoxyethoxy)ethanol, and nearly athermal for mixtures with 2-(2-methoxyethoxy)ethanol and 2-(2-ethoxyethoxy)ethanol.

The V^E values parallel, to some extent, the trend for the excess enthalpies in the systems measured. The C_p^E values are very small and they suggest that the change in H^E with temperature is towards nearly ideal values.

ACKNOWLEDGEMENTS

This work was performed within the frame of the Spanish–French treaty on scientific and technical co-operation. J.C.C. and C.C. gratefully acknowledge the financial support received.

REFERENCES

1 J.C. Cobos and C. Casanova, Fluid Phase Equilibria, 20 (1985) 155.
2 J.C. Cobos and C. Casanova, J. Chem. Thermodyn., 19 (1987) 751.
3 J.C. Cobos, C. Casanova, G. Roux-Desgranges and J.-P.E. Grolier, J. Chem. Thermodyn., 19 (1987) 791.
4 J.C. Cobos, I. García, C. Casanova, G. Roux-Desgranges and J.-P.E. Grolier, Thermochim. Acta, 131 (1988) 73.
5 J.C. Cobos, M.A. Villamañán and C. Casanova, J. Chem. Thermodyn., 16 (1984) 861.