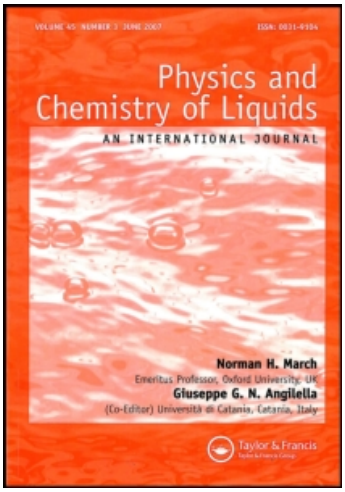

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Thermodynamic Parameters of Binary Liquid Mixtures of Some *n*-Alkoxyethanols with Water at 298.15 K Deduced from Ultrasonic Speed and Viscosity Data

Amalendu Pal[a]; Harsh Kumar[a]
[a] Department of Chemistry, Kurukshetra University, Kurukshetra, India

Online publication date: 27 October 2010

To cite this Article Pal, Amalendu and Kumar, Harsh(2003) 'Thermodynamic Parameters of Binary Liquid Mixtures of Some *n*-Alkoxyethanols with Water at 298.15 K Deduced from Ultrasonic Speed and Viscosity Data', Physics and Chemistry of Liquids, 41: 4, 405 — 421
To link to this Article: DOI: 10.1080/0031910031000136183
URL: http://dx.doi.org/10.1080/0031910031000136183

Physics and Chemistry of Liquids
Vol. 41, No. 4, August 2003, pp. 405–421

Taylor & Francis
Taylor & Francis Group

THERMODYNAMIC PARAMETERS OF BINARY LIQUID MIXTURES OF SOME *n*-ALKOXYETHANOLS WITH WATER AT 298.15 K DEDUCED FROM ULTRASONIC SPEED AND VISCOSITY DATA

AMALENDU PAL* and HARSH KUMAR

Department of Chemistry, Kurukshetra University, Kurukshetra – 136 119, India

(Received 1 December 2002)

A number of different approaches have been proposed to obtain thermodynamic functions like internal pressure, free-volume, energy of vaporization, heat of vaporization etc. of seven binary liquid mixtures. Corresponding excess functions have been computed. The results are explained on the basis of intermolecular interactions.

Keywords: Binary liquid mixtures; Alkoxyethanols; Water; Thermodynamic parameters

INTRODUCTION

Excess thermodynamic properties of *n*-alkoxyethanols containing mixtures are currently attracting considerable interest as the variation of these properties with changing the alkyl chain length as well as the polar head group in *n*-alkoxyethanols provide important information [1–4]. The interest in such studies develops from their different mixing behavior in the presence of a water molecule. Such mixtures are known to exhibit interesting thermodynamic functions which are commonly discussed in terms of molecular interactions. There have been some interesting recent investigations of (amphiphile + water) systems [5–8] designed to provide information about the nature of the amphiphile aggregates. In recent years, it has been found that the internal pressure and free volume in solution thermodynamics are important tools in the study of several chemical reactions and in the investigations of molecular interactions. Pioneering works carried out by Barton [9], Dack [10,11], Hildebrand and Scott [12], Suryanarayana [13] and Pandey *et al*. [14] show the significance of internal pressure and its correlation with other thermodynamic parameters. The internal pressure and free volume of liquids are highly useful in understanding molecular interactions, internal structure, and the aggregation behavior.

*Corresponding author. E-mail: palchem@sify.com

ISSN 0031-9104 print: ISSN 1029-0451 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0031910031000136183

Extensive work has been carried out on measurements of excess molar volume, viscosity, and ultrasonic speed of (amphiphile + water) mixtures in our laboratory and is still in progress. These parameters are required to compute the internal pressure, free volume and other thermodynamic properties. In a continuing effort to collect other thermodynamic quantities in order to extend the available database for these mixtures, we report here several excess thermodynamic properties like excess internal pressure (P_{int}^{E}), excess free volume (V_f^E), excess energy of vaporization (U_{vap}^{E}), heat of vaporization (H_{vap}), cohesive energy density (ced), solubility parameter (δ). Two different approaches have been proposed to obtain the internal pressure values. The results are explained in terms of the nature of molecular interactions during mixing.

WORKING EQUATIONS

Internal pressure may be estimated from the well-known thermodynamic equation of state

$$P = T(\partial P/\partial T)_V - (\partial U/\partial V)_T \tag{1}$$

where U is the internal energy, V is the volume and T is the temperature.

For a liquid system the magnitude of the term, $(\partial P/\partial T)_V$ known as the thermal pressure coefficient multiplied by the temperature is thousand times the magnitude of P, which becomes negligible by comparison [11], hence the Eq. (1) becomes

$$T(\partial P/\partial T)_V = (\partial U/\partial V)_T \tag{2}$$

By making use of values of α (coefficient of thermal expansion) and κ_{T} (isothermal compressibility), internal pressure can be expressed as [15]

$$P_{\text{int}} = (\partial U/\partial V)_T = (\alpha T/\kappa_T) - P \tag{3}$$

At zero pressure, the above equation reducces to

$$P_{\text{int}} = \alpha T/\kappa_T \tag{4}$$

From this relation the ideal values of P_{int} for multicomponent system is given by the additivity of internal pressures of pure substances in the mole fraction scale

$$(P_{\text{int}})_{\text{id}} = \sum_{i=1} x_i (P_{\text{int}})_i \tag{5}$$

where x_i is the mole fraction and $(P_{\text{int}})_i$ is the internal pressure of tile ith component.

On the basis of dimensional analysis using free volume concept an alternative method for the calculation of internal pressure was suggested by Suryanarayana [13,16] from the knowledge of ultrasonic velocity u, density ρ, and, viscosity η. According to Suryanarayana, internal pressure P_{int}, free volume V_f and temperature T can be used to define the state of liquid and gave the following relation

$$P_{\text{int}} = bRT(K\eta/u)^{1/2}(\rho^{2/3}/M^{7/6}) \tag{6}$$

where b is the packing factor in liquids, K is a dimensional constant having a value of 4.28×10^9 and independent of temperature and nature of the liquid and η the viscosity. The other symbols have their usual meanings. From Eq. (6) we can estimate the value of P_{int} from a knowledge of η, ρ, and u and it does not require the values of α and κ_T. For liquid mixtures, Eq. (6) can be written as

$$(P_{\text{int}})_{\text{mix}} = bRT(K\eta_{\text{mix}}/u_{\text{mix}})^{1/2}(\rho^{2/3}M_{\text{mix}}^{7/6}) \tag{7}$$

where $M_{\text{mix}}(=\sum x_i M_i)$ is the molar mass of the mixture.

The above Eq. (7) has one advantage in the sense that internal pressure of a liquid system can be calculated directly from the experimental density and speed of sound values.

The excess internal pressure P_{int}^E of liquid mixture is given as

$$P_{\text{int}}^E = (P_{\text{int}})_{\text{mix}} - \sum x_i(P_{\text{int}})_i \tag{8}$$

$(P_{\text{int}})_{\text{mix}}$ is internal pressure of the mixture that includes all types of interactions.

The values of internal pressure obtained from speed of sound, density, and viscosity data have been used to deduce the excess enthalpy of binary liquid mixture using the relation [17]

$$H^E = -\Delta(P_{\text{int}}V) = \sum x_i(P_{\text{int}})_i V_i - (P_{\text{int}})_{\text{mix}}V_{\text{mix}} \tag{9}$$

where V is the molar volume.

The energy of vaporization U_{vap}, may be obtained from P_{int} values using the relation [18]

$$U_{\text{vap}} = P_{\text{int}}V \tag{10}$$

The ideal values of energy of vaporization can be calculated by putting ideal values of internal pressure and molar volume as

$$(U_{\text{vap}})_{id} = (P_{\text{int}})_{\text{id}}V_{\text{id}} \tag{11}$$

Similarly,

$$(U_{\text{vap}})_{\text{mix}} = (P_{\text{int}})_{\text{mix}}V_{\text{mix}} \tag{12}$$

and excess energy of vaporization U_{vap}^E is obtained through the expression

$$U_{\text{vap}}^E = (U_{\text{vap}})_{\text{mix}} - (U_{\text{vap}})_{\text{id}} \tag{13}$$

Heat of vaporization H_{vap} is given as

$$H_{\text{vap}} = U_{\text{vap}} + RT \tag{14}$$

Since RT is constant, the value of excess energy of vaporization is equal to the excess heat of vaporization.

The cohesive energy of density may be calculated by the relation

$$\text{ced} = U_{\text{vap}}/V = P_{\text{int}} \tag{15}$$

Since internal pressure is the result of the forces of attraction and repulsion between molecules of liquids. This definition resembles the well-known definition of solubility

parameter, δ. It call be expressed [19] in terms of cohesive energy density which is related to internal pressure as

$$\delta = (\text{ced})^{1/2} = (P_{\text{int}})^{1/2} \tag{16}$$

The free volume V_f, of a molecule in liquid has been the subject of intensive investigation in the past [20–22]. As the free-volume depends only on the internal pressure of the medium at a given temperature, we thought it worthwhile to calculate the free volume of these systems. Although several workers [23–26] discussed thoroughly a reasonable partition function for liquids and as a result, the free volume V_f in a liquid is defined by the relation

$$V_f = [bRT/(P + (\partial U/\partial V)_T]^3 (1/V^2) \tag{17}$$

$(\partial U/\partial V)_T$ is the internal pressure and P is negligible in comparison to the internal pressure.

Therefore,

$$V_f = [bRT/P_{\text{int}}]^3 (1/V^2) \tag{18}$$

An alternative approach was derived by Suryanarayana and Kuppusami [27] to calculate the free volume

$$V_f = (Mu/K\eta)^{3/2} \tag{19}$$

All the symbols have their usual meanings.

Equations (18) and (19) have been used to compute the free volume. The excess free volume V_f^E can then be calculated as

$$V_f^E = V_f - \sum x_i V_{f,i} \tag{20}$$

where $V_{f,i}$ is the free volume of the ith component, and V_f is the free volume of the mixture.

RESULTS AND DISCUSSION

The present investigation considered seven binary liquid mixtures: 2-methoxyethanol +; 2-(2-methoxyethanol) +; 2-(2-ethoxyethanol) +; 2-(2-butoxyethanol) +; 2-{2-(2-methoxyethoxy)ethoxy}ethanol +; 2-{2-(2-methoxyethoxy)ethoxyl}ethanol +; 2-{2-(2-methoxyethoxy)ethoxy}ethanol + water. Literature values [1,5–8,28–36] of density ρ, viscosity η, ultrasonic speeds u of those systems at 298.15 K are given in Table I. Also listed their different thermodynamic parameters e.g. thermal expansion coefficient α, heat capacity C_p, and isothermal expansion compressibility κ_T of pure liquid components. Internal pressure values for all the pure liquid components calculated from Eqs. (4) and (6) are listed in Table I. The calculated values of U_{vap}^E, H_{vap}, ced, and δ using Eqs. (13)–(16) for the present binary liquid mixtures are included in Table III. From the internal pressure of pure liquid components, the internal pressure of the ideal mixture is calculated by Eq. (5). Thus, we obtain two sets of $(P_{\text{int}})_{\text{id}}$ values; first one from Eqs. (5) and (4) and second one from Eqs. (5) and (6), respectively. These values axre recorded in Table II. Due to lack of experimental data of α and κ_T for the present mixtures, only

TABLE I Thermodynamic parameters of pure liquid components at 298.15 K

Component	$\rho \times 10^{-3}$ (kgm^{-3})	$\eta \times 10^{-3}$ ($kgm^{-1}s^{-1}$)	u ($m\,s^{-1}$)	α ($k\,K^{-1}$)	C_p	κ_T (TP^{-1})	P_{int} (atm)		U_{vap} ($J\,mol^{-1}$)	H_{vap} ($J\,mol^{-1}$)	$ced \times 10^{-6}$ ($J\,m^{-3}$)	$\delta \times 10^{-3}$ ($J\,m^{-3})^{-1/2}$	$V_f \times 10^{-3}$ ($m^3\,mol^{-1}$)	
							Eq. (4)	*Eq. (6)*					*Eq. (19)*	*Eqs. (6) and (18)*
H_2O	0.997048 [28]	0.89025 [29]	1496.687 [30]	0.257 [28]	75.292 [31]	452.47	1671.33	26670.92	48829.20	51308.20	2702.43	51.98	0.0188	0.0188
$CH_3OC_2H_4OH$	0.96002 [6]	1.541 [32]	1339.89 [6]	0.9198[a]	176.4 [33]	693.54	3902.47	6696.65	53873.85	56262.67	709.81	26.64	0.0608	0.0596
$CH_3(OC_2H_4)_2OH$	1.0176 [7]	4.046 [7]	1423.1 [34]	0.849[b]	271.1 [29]	578.83	4315.93	6020.35	72024.38	74503.20	610.01	24.70	0.0310	0.0392
$C_2H_5(OC_2H_4)_2OH$	0.9839 [7]	4.424 [7]	1385.2 [34]	0.846 [5]	298.1 [1]	627.31	3968.32	5671.91	78373.23	80852.05	574.71	23.97	0.0371	0.0339
$C_4H_9(OC_2H_4)_2OH$	0.9479 [7]	5.503 [7]	1356.4 [34]	0.843 [5]	358.4 [35]	674.59	3677.10	4988.58	86508.71	88987.53	505.47	22.48	0.0286	0.0305
$CH_3(OC_2H_4)_3OH$	1.0430 [7]	6.964 [7]	1456.5 [8]	0.828 [1]	358.0 [1]	541.84	4496.53	5772.14	92076.04	94554.86	584.86	24.18	0.0227	0.0256
$C_2H_5(OC_2H_4)_3OH$	1.0161 [7]	7.210 [7]	1417.3 [8]	0.856 [35]	389.0 [35]	588.45	4280.38	5119.66	90991.01	93469.83	518.75	22.78	0.0234	0.0282
$C_4H_9(OC_2H_4)_3OH$	0.9868 [7]	9.361 [7]	1398.8 [36]	0.848 [35]	450.0 [35]	617.52	4040.76	4935.89	104547.79	107026.61	500.13	22.36	0.0193	0.0219

[a]From [6]; [b]Calculated from measured densities.

TABLE II Ideal and excess internal pressures for (*n*-alkoxyethanol + water) systems at 298.15 K

x_1	$(P_{int})_{id}$ (atm)		P^E_{int} (atm)	x_1	$(P_{int})_{id}$ (atm)		P^E_{int} (atm)
	Eqs. (5) and (4)	*Eqs. (5) and (6)*			*Eqs. (5) and (4)*	*Eqs. (5) and (6)*	
			2-Methoxyethanol (1) + water (2)				
0.0199	1715.73	26273.43	1684.06	0.3977	2558.65	18727.15	−907.38
0.0398	1760.13	25875.94	2949.91	0.4590	2695.42	17502.73	−1621.62
0.0598	1804.75	25476.46	3443.81	0.5167	2824.16	16350.21	−2018.21
0.0797	1849.15	25078.97	3708.11	0.5798	2694.95	15089.84	−2334.66
0.0983	1890.65	24707.45	3481.31	0.6393	3097.70	13901.37	−2262.80
0.1303	1962.05	24068.27	3445.50	0.6999	3232.91	12690.93	−2132.93
0.1705	2051.74	23265.31	2871.19	0.7599	3366.78	11492.47	−1964.98
0.2203	2162.85	22270.59	2053.92	0.8205	3501.98	10282.03	−1743.45
0.2797	2295.38	21084.12	913.15	0.8732	3619.57	9229.39	−1258.12
0.3393	2428.36	19893.65	−284.91	0.9259	3737.15	8176.74	−777.57
			2-(2-Methoxyethoxy)ethanol (1) + water (2)				
0.0435	1786.37	25772.62	5195.82	0.2342	2290.69	21834.56	2230.92
0.0495	1802.24	25648.72	5690.38	0.2830	2419.75	20826.81	981.41
0.0618	1834.76	25394.71	5954.25	0.3367	2561.77	19717.87	17.57
0.0705	1857.77	25215.05	6093.31	0.4449	2847.91	17483.48	−2094.29
0.0817	1887.39	24983.77	5952.81	0.5842	3216.31	12896.99	−2801.89
0.1063	1952.45	24475.76	5626.69	0.6670	3435.28	11201.58	−2630.22
0.1226	1995.56	24139.16	5252.75	0.7491	3652.40	11201.58	−2398.36
0.1460	2057.44	23655.94	4608.09	0.8389	3889.89	9347.16	−2358.90
0.1791	2144.98	22972.40	3548.63	0.9582	4205.39	6883.54	−234.32
			2-(2-Ethoxyethoxy)ethanol (1) + water (2)				
0.0430	1770.10	25767.96	7438.28	0.1913	2110.74	22653.81	3274.10
0.0521	1791.00	25576.87	7355.66	0.2485	2242.13	21452.67	1780.22
0.0653	1821.32	25299.69	7603.34	0.3116	2387.07	20127.63	−347.67
0.0805	1856.24	24980.50	7624.09	0.3975	2584.38	18323.81	−1910.05
0.1008	1902.86	24554.22	6678.55	0.5108	2844.63	15944.63	−3302.64
0.1210	1949.26	24130.04	6076.27	0.6172	3089.03	13710.33	−3455.40
0.1354	1982.34	23827.65	5650.41	0.7235	3333.20	11478.14	−2811.49
0.1531	2023.00	23455.97	5250.92	0.7818	3467.11	10253.89	−2333.16
0.1695	2060.67	23111.59	4528.79	0.8860	3706.46	8065.80	−1546.24
			2-(2-Butoxyethoxy)ethanol (1) + water(2)				
0.0016	1674.54	26636.23	1637.20	0.0778	1827.38	24984.04	7506.44
0.0020	1675.34	26627.56	1899.29	0.1025	1876.92	24448.48	9282.55
0.0057	1682.76	26547.33	3327.29	0.1352	1942.51	23739.47	5134.47
0.0091	1689.58	26473.61	4270.49	0.1713	2014.92	22956.73	6021.55
0.0107	1692.79	26438.92	4448.74	0.2244	2121.42	21805.40	683.30
0.0144	1700.21	26358.69	5217.22	0.2695	2211.88	20827.53	−650.43
0.0168	1705.02	26306.06	5598.96	0.3081	2299.31	19990.59	−1781.67
0.0191	1709.65	26256.79	5880.57	0.4136	2500.92	17703.11	−3922.55
0.0209	1713.25	26217.76	6269.95	0.4994	2673.01	15842.76	−4502.28
0.0232	1717.86	26167.89	6449.26	0.5582	2790.95	14567.84	−4839.96
0.0340	1739.52	25933.72	7451.78	0.6696	2014.40	12152.42	−4103.34
0.0398	1751.16	25807.96	7887.29	0.7403	3156.20	10619.48	−3371.84
0.0408	1753.16	25786.28	8157.11	0.8806	3437.61	7577.45	−1809.44
0.0477	1767.00	25636.67	8159.85	0.9321	3540.91	6460.81	−1403.27
0.0588	1789.27	25396.00	8250.60				
			2-{2-(2-Methoxyethoxy)ethoxy}ethanol (1) + water(2)				
0.0010	1674.15	26650.02	−7538.16	0.2890	2487.81	20631.17	1040.68
0.0025	1678.39	26618.67	−5780.65	0.3191	2572.85	20002.12	279.44
0.0040	1682.63	26587.32	−4454.54	0.3583	2683.60	19182.19	−395.70
0.0082	1694.49	26499.55	−1065.14	0.4019	2806.78	18271.70	−1931.23
0.0147	1712.86	26363.71	2178.90	0.4415	2918.65	17444.11	−1991.60
0.0380	1778.69	25876.77	7739.00	0.4719	3004.54	16808.79	−2247.61
0.0514	1816.54	25596.72	8716.85	0.5187	3306.27	14576.80	−3630.47

(*continued*)

TABLE II Continued

x_1	$(P_{int})_{id}$ (atm)		P^E_{int} (atm)	x_1	$(P_{int})_{id}$ (atm)		P^E_{int} (atm)
	Eqs. (5) and (4)	*Eqs. (5) and (6)*			*Eqs. (5) and (4)*	*Eqs. (5) and (6)*	
0.0609	1843.38	25698.19	9142.64	0.5754	3296.95	14645.76	−3643.04
0.0711	1872.20	25185.02	9273.91	0.5898	3337.63	14344.82	−3388.99
0.0854	1912.60	24886.16	9130.89	0.6561	3524.94	12959.23	−2977.71
0.1098	1981.53	24376.23	7875.44	0.7082	3672.14	11870.40	−2775.35
0.1217	2015.15	24127.54	8002.65	0.7359	3750.39	11291.51	−3002.17
0.1415	2071.09	23713.74	6683.99	0.7820	3880.64	10328.07	−2017.85
0.1640	2134.66	23243.52	5749.02	0.8142	3971.61	9655.13	−2217.82
0.1852	2194.55	22800.47	5017.17	0.8802	4158.07	8257.81	−1640.18
0.2063	2254.17	22359.50	3986.90	0.9349	4312.61	7132.65	−552.57
0.2565	2395.99	21310.38	2338.05	0.9739	4442.79	6317.60	−518.69
			2-{2-(2-Ethoxyethoxy)ethoxy}ethanol (1) + water (2)				
0.0004	1672.37	26662.30	−7968.56	0.2463	2313.94	21362.85	1870.55
0.0016	1675.50	26636.44	−6415.52	0.2778	2396.12	20683.98	393.72
0.0021	1676.81	26625.66	−5678.88	0.3085	2476.22	20022.36	−437.65
0.0041	1682.02	26582.56	−3439.65	0.3551	2597.80	19018.07	−1926.77
0.0066	1688.55	26528.68	−1316.73	0.4041	2725.65	17962.06	−2699.72
0.0099	1697.16	26457.56	1034.55	0.4405	2820.62	17177.59	−2860.73
0.0144	1708.90	26360.58	3400.79	0.4693	2895.76	16556.91	−3198.40
0.0215	1727.42	26207.57	5831.60	0.5172	3020.73	15524.61	−4028.60
0.0337	1759.25	25944.64	7989.21	0.5556	3120.92	14697.04	−4170.07
0.0418	1780.39	25770.08	9142.33	0.6038	3246.67	13658.27	−4106.62
0.0525	1808.30	25539.48	9458.81	0.6420	3346.34	12835.01	−4186.81
0.0613	1831.26	25349.83	9607.53	0.6811	3448.35	11992.36	−3436.98
0.0714	1857.61	25132.16	9607.11	0.7486	3624.96	10537.65	−2869.06
0.0827	1887.10	24888.63	9400.98	0.7756	3694.91	9955.76	−3082.51
0.0914	1909.79	24701.13	8998.01	0.8113	3788.05	9186.38	−2341.53
0.1127	1965.37	24242.09	8038.46	0.8352	3850.41	8671.31	−1845.71
0.1437	2046.25	23574.00	7025.61	0.8804	3968.34	7697.19	−1666.40
0.1746	2126.87	22908.07	4844.89	0.9549	4162.71	6091.62	−532.34
0.2059	2208.53	22233.52	3453.32	0.9740	4212.55	5679.99	−164.71
			2-{2(2-Butoxyethoxy)ethanol (1) + water (2)				
0.0045	1681.99	26573.11	−488.48	0.3062	2396.85	20015.65	−1479.35
0.0099	1694.78	26455.74	3187.12	0.3418	2481.20	19241.89	−2477.98
0.0134	1703.08	26379.67	4691.74	0.4033	2626.92	17905.18	−3976.48
0.0177	1713.27	26286.21	6258.24	0.4651	2773.35	16561.96	−4638.12
0.0207	1720.37	26221.01	7369.94	0.4965	2847.75	15879.48	−4964.55
0.0247	1729.85	26134.06	8022.39	0.5465	2966.22	14792.73	−4928.46
0.0316	1746.20	25984.09	9215.32	0.5766	3037.54	14138.50	−5247.90
0.0432	1773.69	25731.97	9869.00	0.6303	3164.78	12971.33	−4203.02
0.0573	1807.10	25425.50	10266.00	0.6961	3320.69	11541.17	−3756.37
0.0684	1833.40	25184.24	9927.25	0.7515	3451.96	10337.04	−3471.44
0.0839	1870.12	24847.35	9054.71	0.7845	3530.15	9619.79	−2777.50
0.1079	1926.99	24325.71	7652.76	0.8367	3653.83	8485.22	−2527.23
0.1420	2007.79	23584.54	5800.20	0.8824	3762.11	’1491.93	−2565.26
0.1845	2108.49	22660.81	2930.28	0.9209	3853.34	6655.13	−1609.94
0.2152	2181.23	21993.54	1840.68	0.9518	3926.55	5983.52	−978.46
0.2686	2307.76	20832.89	−701.06	0.9713	3972.76	5559.69	−589.89

Eq. (7) has been used to obtain $(P_{\text{int}})_{\text{mix}}$ using either our experimental values [7,8,34, 36–38] or literature values [32] of ρ, u, and η. From the values of $(P_{\text{int}})_{\text{id}}$ (Table II) and $(P_{\text{int}})_{\text{mix}}$ (from Eq. (7)) the excess internal pressure, P^E_{int} was calculated using Eqs. (7) and (8). The calculated values are recorded in Table II and are graphically represented in Figure 1.

TABLE III Thermodynamic parameters of (*n*-alkoxyethanol + water) systems at 298.15 K

x_1	U_{vap} (J mol^{-1})	U^E_{vap} (J mol^{-1})	H_{vap} (J mol^{-1})	$ced \times 10^6$ (J m^{-3})	$\delta \times 10^{-3}$ (J m^{-3})$^{1/2}$
		2-Methoxyethanol (1) + water (2)			
0.0199	54314.73	5386.94	56793.55	2832.79	53.22
0.0398	59242.33	10215.93	61721.15	2920.78	54.04
0.0598	62719.65	13594.16	65198.47	2930.35	54.13
0.0797	65701.05	16476.97	68179.88	2916.85	54.01
0.0983	67346.47	18030.23	69825.29	2856.23	53.44
0.1303	70831.98	21357.20	73310.80	2787.83	52.80
0.1705	73445.37	23771.40	75924.19	2648.28	51.96
0.2203	75562.05	25641.34	78040.87	2464.68	49.65
0.2797	76236.77	26021.76	78715.79	2228.87	47.21
0.3393	75137.20	24626.89	77616.02	1986.86	44.57
0.3977	74747.95	23948.29	77226.77	1805.59	42.49
0.4590	72716.32	21612.94	75195.14	1609.15	40.11
0.5167	70836.19	19446.92	73315.01	1452.19	38.11
0.5798	68138.01	16436.10	70616.83	1292.42	35.95
0.6393	66571.43	14574.72	69050.25	1179.28	34.34
0.6999	64466.81	12169.85	66945.63	1069.79	32.71
0.7599	61828.98	9234.74	64307.80	965.37	31.07
0.8205	58731.00	5$36.51	61209.82	865.17	29.41
0.8732	57531.98	4375.68	60010.10	807.69	28.42
0.9259	55911.97	2495.23	58390.79	749.72	27.38
		2-(2-Methoxyethoxy)ethanol (1) + water (2)			
0.0435	69221.92	19383.73	71700.74	3137.38	56.02
0.0495	71822.87	21845.51	74301.69	3175.43	56.35
0.0618	75497.75	25235.09	77976.57	3176.43	56.36
0.0705	77993.44	27528.98	80472.26	3172.36	53.32
0.0817	80379.76	29655.51	82858.58	3134.65	55.99
0.1063	85349.38	34054.54	87828.20	3050.13	55.23
0.1226	87988.12	36315.19	90466.94	2978.15	54.57
0.1460	91081.21	38865.52	93560.03	2863.85	53.51
0.1791	94125.41	41141.96	96604.23	2687.24	51.84
0.2342	98637.45	44375.93	101116.30	2438.43	49.38
0.2830	100105.90	44712.48	102584.70	2209.72	47.01
0.3367	101338.40	44699.37	103817.20	1999.69	44.72
0.4449	96019.27	36870.53	98498.09	1559.31	39.49
0.5842	90532.31	28152.49	93011.13	1196.14	24.59
0.6670	87488.83	23188.44	89967.65	1040.25	32.25
0.7491	82478.30	16273.58	84957.12	891.99	29.87
0.8389	82266.59	13978.95	84745.41	809.41	28.45
0.9582	76685.16	5630.34	79163.98	673.73	25.96
		2-(2-Ethoxyethoxy)ethanol (1) + water (2)			
0.0430	76455.64	26356.05	78934.66	3364.22	58.01
0.0521	80212.88	29844.43	82691.70	3380.79	58.14
0.0653	85161.87	34403.44	87640.69	3380.86	58.15
0.0805	88827.39	37619.90	91306.21	3303.66	57.48
0.1008	93893.41	42086.17	96372.23	3218.30	56.73
0.1210	98104.03	45700.00	100582.90	3117.33	55.83
0.1354	100857.80	48028.38	103336.60	3045.43	55.19
0.1531	102250.20	48897.82	104729.00	2908.73	53.93
0.1695	103759.60	49922.69	106238.40	2800.66	53.93
0.1913	106518.70	52037.75	108997.50	2691.22	51.88
0.2485	108941.90	52771.02	111420.70	2354.07	48.52
0.3116	111403.30	53368.21	113882.20	2073.31	45.53
0.3975	106352.10	45779.18	108830.90	1663.12	40.78
0.5108	99256.95	25336.65	101735.80	1280.95	35.79

(*continued*)

TABLE III Continued

x_1	U_{vap} ($J\,mol^{-1}$)	U^E_{vap} ($J\,mol^{-1}$)	H_{vap} ($J\,mol^{-1}$)	$ced \times 10^6$ ($J\,m^{-3}$)	$\delta \times 10^{-3}$ $(J\,m^{-3})^{1/2}$
0.6172	93 768.43	26704.65	96247.25	1039.08	32.23
0.7235	90458.92	20254.62	93937.74	878.15	29.63
0.7818	88301.81	16375.09	90780.63	802.57	28.33
0.8860	80974.41	5969.20	83453.23	660.59	25.70
		2-(2-Butoxyethoxy)ethanol (1) + water (2)			
0.0016	52434.37	3544.89	54913.19	2864.81	5352
0.0020	53073.74	4169.18	55552.56	2890.48	53.76
0.0057	57222.80	8178.82	59701.62	3027.05	55.02
0.0091	60442.29	11270.20	62921.11	3115.15	55.81
0.0107	61459.97	12227.60	63938.79	3129.69	55.94
0.0144	64568.19	15196.41	67047.01	3199.43	56.56
0.0168	663 82.97	16920.75	68861.79	3232.84	56.86
0.0191	67967.36	18418.48	70446.18	3256.32	57.06
0.0209	69580.33	19963.63	72059.25	3291.82	57.37
0.0232	70976.53	21273.17	73455.35	3304.93	57.49
0.0340	78035.78	27925.48	80514.60	3382.79	58.16
0.0398	81684.38	31355.54	84163.20	3414.17	58.43
0.0408	82794.65	32428.13	85273.47	3439.31	58.65
0.0477	85931.87	35305.36	88410.69	3424.43	58.52
0.0588	91 158.51	40113.75	93637.33	3409.24	58.39
0.0778	97319.27	45558.61	99798.09	3292.10	57.38
0.1025	103514.80	50823.48	105993.60	3113.82	55.80
0.1352	111576.50	57652.99	114055.30	2925.65	54.09
0.1713	114662.60	59378.93	117141.40	2632.25	51.31
0.2244	117519.80	60235.27	119998.60	2278.67	57.74
0.2695	119415.00	60431.14	121893.60	2044.44	45.22
0.3081	118598.20	58159.90	121077.00	1845.02	42.95
0.4136	112288.90	47875.50	114767.80	1396.32	37.37
0.4994	107583.50	39937.14	110062.30	1149.07	33.90
0.5582	101238.00	31376.10	103716.80	985.68	31.40
0.6696	97819.65	23760.25	100298.50	815.57	28.56
0.7403	96101.66	19378.31	98580.48	734.37	27.10
0.8806	89132.82	7123.01	91611.64	584.44	24.18
0.9321	82245.02	1705.26	84273.84	512.46	22.64
		2-{2-(2-Methoxyethoxy)ethoxy}ethanol (1) + water (2)			
0.0010	35238.21	−13634.24	37717.03	1936.51	44.01
0.0025	38827.20	−10110.12	41306.02	2111.41	45.95
0.0040	41671.23	−7330.96	44150.05	2242.60	47.36
0.0082	58791.30	−392.59	51270.12	2551.63	50.51
0.0147	57724.29	8259.36	60203.11	2892.08	53.78
0.0380	77314.55	26841.97	79793.38	3363.54	58.00
0.0514	84845.02	33792.94	87323.84	3429.19	58.56
0.0609	88335.37	36872.43	90814.19	3398.40	58.30
0.0711	92528.47	40624.42	95007.29	3384.12	58.17
0.0854	97431.59	44909.11	99910.41	3331.19	57.72
0.1098	104187.30	50609.59	106666.10	3205.06	56.61
0.1217	106604.90	52512.56	109083.70	3125.37	55.90
0.1415	110791.00	55842.41	113269.10	3011.60	54.88
0.1640	114209.50	58287.78	116688.30	2866.02	53.54
0.1852	117324.40	60485.87	119803.20	2744.45	52.39
0.2063	118381.90	60630.92	120860.80	2593.28	50.92
0.2565	121823.00	61900.94	124301.80	2316.30	48.13
0.2890	120777.10	59449.52	123255.90	2114.57	45.98
0.3191	120974.20	58344.90	123453.00	1972.83	44.42
0.3583	121653.40	57328.82	124132.20	1820.85	42.67

(*continued*)

TABLE III Continued

x_1	U_{vap} ($J\,mol^{-1}$)	U^E_{vap} ($J\,mol^{-1}$)	H_{vap} ($J\,mol^{-1}$)	$ced \times 10^6$ ($J\,m^{-3}$)	$\delta \times 10^{-3}$ $(J\,m^{-3})^{1/2}$
0.4019	114722.40	48512.29	117201.20	1572.91	39.66
0.4415	116453.40	48530.68	118932.20	1483.32	38.51
0.4719	115365.40	46128.00	117844.20	1393.44	37.33
0.5187	108532.10	34765.99	111011.00	1109.14	33.30
0.5754	108572.20	34858.73	111051.00	1114.85	33.39
0.5898	102481.00	28144.84	104959.90	1030.81	32.11
0.6561	101547.60	24344.14	104026.40	933.58	30.55
0.7082	100818.50	18640.10	103297.30	844.76	29.06
0.7359	98096.71	20163.97	100575.50	839.92	28.98
0.7820	95000.58	12352.34	97479.40	757.19	27.52
0.8142	98791.69	14750.91	101270.50	753.60	27.45
0.8802	94417.66	7522.58	96896.48	672.36	25.93
0.9349	87819.01	−1441.67	90297.83	592.65	24.34
0.9739	90321.59	−625.71	92800.41	587.57	24.27
		2-{2-(2-Ethoxyethoxy)ethoxy}ethanol (1) + water (2)			
0.0004	34332.80	−14513.26	36811.63	1894.14	43.52
0.0016	37488.93	−11407.73	39967.75	2048.88	45.26
0.0021	38986.17	−9931.57	41464.99	2122.43	46.07
0.0041	43745.12	−5256.94	46223.94	2344.96	48.42
0.0066	48752.04	−535.43	51050.86	2554.60	50.54
0.0099	54285.89	5039.29	56764.71	2785.64	52.78
0.0144	60723.61	11287.28	63202.43	3015.57	54.91
0.0215	68708.84	18973.16	71187.66	3246.37	56.98
0.0337	78872.02	28261.96	81350.84	3437.64	58.63
0.0418	85369.66	34778.10	87848.48	3537.50	59.48
0.0525	91182.38	40139.69	93661.20	3546.20	59.55
0.0613	95704.72	44291.00	98183.54	3452.05	59.52
0.0714	100414.10	48574.56	102892.90	3519.96	59.33
0.0827	105007.10	52691.09	107485.90	3474.39	58.94
0.0914	107677.90	54995.09	110156.70	341457	58.43
0.1127	113716.40	60135.55	116195.20	3270.83	57.19
0.1437	119601.70	64713.88	122080.60	3026.68	55.02
0.1746	124533.70	68363.05	127032.50	2812.07	53.03
0.2059	127963.10	70452.77	130441.90	2602.71	51.02
0.2463	130640.00	71426.38	133118.80	2354.12	48.52
0.2778	129104.80	68563.04	131583.60	2135.70	46.21
0.3085	129573.70	67737.55	132052.50	1984.42	44.55
0.3551	125 844.90	62044.01	128323.70	1731.78	41.61
0.4041	124635.40	58768.62	127414.20	1549.50	39.36
0.4405	117708.80	50307.36	120187.70	1365.32	36.95
0.4693	115205.10	46589.40	117684.00	1268.95	35.62
0.5172	114620.50	43985.26	117099.40	1164.83	34.13
0.5556	111474.00	39219.72	113952.80	1066.65	32.66
0.6038	108569.90	34823.42	111048.70	967.82	31.11
0.6420	103361.60	27734.55	106110.50	876.28	29.60
0.6811	107919.10	30373.52	110397.90	866.87	29.44
0.7486	105096.00	24704.51	107574.90	777.02	27.88
0.7756	100745.40	15665.68	103224.30s	696.43	26.39
0.8113	103100.80	17710.37	105579.60	693.55	26.34
0.8352	97195.59	19058.08	99674.71	691.60	26.30
0.8804	95504.89	9556.43	97983.71	611.07	24.72
0.9549	88381.00	−708.52	90859.82	525.48	22.92
0.9740	89319.44	−575.37	91798.26	521.59	22.84
		2-{2-(2-Butoxyethoxy)ethoxy}ethanol (1) + water (2)			
0.0045	49923.41	843.48	52402.23	2643.03	51.41
0.0099	59693.87	10313.06	62172.59	3003.56	54.80

(*continued*)

TABLE III Continued

x_1	U_{vap} ($J\,mol^{-1}$)	U^E_{vap} ($J\,mol^{-1}$)	H_{vap} ($J\,mol^{-1}$)	$ced \times 10^6$ ($J\,m^{-3}$)	$\delta \times 10^{-3}$ $(J\,m^{-3})^{1/2}$
0.0134	65286.64	15710.81	67765.46	3182.53	56.41
0.0177	71038.80	21223.38	73517.62	3335.04	57.75
0.0207	74369.92	24387.35	76848.74	3403.50	58.34
0.0247	79113.24	28907.79	81592.06	3503.11	59.19
0.0316	85064.76	34474.85	87453.58	3566.58	59.72
0.0432	95094.17	43857.93	97572.99	3659.55	60.49
0.0573	103386.80	51364.95	105865.60	3616.44	60.14
0.0684	109016.70	56376.31	111495.50	3557.67	59.65
0.0839	117400.60	63896.60	119879.40	3502.48	59.18
0.1079	123093.60	68252.35	125572.40	3240.22	56.92
0.1420	132017.10	75365.88	134585.90	2977.41	54.57
0.1845	135777.20	76667.92	138256.00	2593.05	50.92
0.2152	140453.40	79638.58	142932.20	2415.00	49.14
0.2686	139288.30	75493.10	141767.10	2039.86	45.16
0.3062	141689.50	75799.22	144168.30	1878.19	43.34
0.3418	139681.90	71808.05	142160.70	1698.60	41.21
0.4033	132677.50	61377.02	135156.30	1411.33	37.57
0.4651	127926.30	53182.37	130405.10	1208.18	34.76
0.4965	123788.00	47924.55	126266.80	1105.96	33.26
0.5465	121503.40	42223.96	123982.20	999.50	31.61
0.5766	126212.60	45256.11	128691.50	990.92	31.48
0.6303	122359.40	38410.79	124838.20	888.45	29.81
0.6961	118633.90	31019.01	121112.70	788.79	28.09
0.7515	112037.00	21335.28	114515.80	965.66	26.38
0.7845	116051.60	23511.15	118530.40	693.30	26.33
0.8367	107103.40	11654.44	109582.20	603.69	24.57
0.8824	111815.40	13820.12	114294.20	600.52	24.51
0.9209	98979.74	−1160.71	101458.60	511.20	22.61
0.9518	101229.30	−632.85	103708.10	507.14	22.52
0.9713	102429.90	−518.81	104908.70	503.56	22.44

The calculated values of $(P_{\text{int}})_{\text{mix}}$ decreases regularly from its high water value to the much lower value of ether. That is, the chemical or specific interaction increase with the addition of amphiphile to water, thereby causing a breakdown of the less dense hydrogen-bonded structures of water, or breakdown of self-associated amphiphile aggregates, or both, and hence contribute a denser packing of molecules through hydrogen bonding.

Previously reported values of V^E_m and $K^E_{s,m}$ are found to be negative for all the systems which suggests the association through intermolecular hydrogen bonding between the water and the amphiphile molecules. Study of Table II reveals that P^E_{int} is positive and negative at low and high concentrations of ether for all the systems. Further, it shows that, with the addition of amphiphile to water, deviations from ideality in internal pressure are observed, which are maximum in the water-rich region ($x_1 \sim 0.04-0.07$). It has been established that the sign and magnitude of excess function give a good estimate of the strength of the unlike interaction in a binary mixtures. We can thus make an assumption that strong intermolecular unlike interactions between amphiphile and water are predominant at low and high concentrations of amphiphile. The positive values of the P^E_{int} in water-rich region would imply nonrandom mixing and predict a slight enhancement of the three-dimensional water-structure, followed by a progressive destructuring; the ether functions do not seem to play a prominent role. The positive values of P^E_{int} might also arise due to the fact that the amphiphile

TABLE IV Excess free volumes for (*n*-alkaoxyethonol + water) system at 298.15 K

x_1	$V_f^E \times 10^6$ (m^3 mol^{-1})		x_1	$V_f^E \times 10^6$ (m^3 mol^{-1})	
	Eqs. (6) and (18)	*Eq. (19)*		*Eqs. (6) and (18)*	*Eq. (19)*
		2-Methoxyethanol (1) + water (2)			
0.0199	−0.0053	−0.0053	0.3977	−0.0236	−0.0237
0.0398	−0.0088	−0.0086	0.4590	−0.0239	−0.0243
0.0598	−0.0109	−0.0108	0.5167	−0.0240	−0.0244
0.0797	−0.0127	−0.0124	0.5798	−0.0232	−0.0240
0.0983	−0.0138	−0.0137	0.6393	−0.0227	−0.0231
0.1303	−0.0158	−0.0155	0.6999	−0.0212	−0.0216
0.1705	−0.0177	−0.0174	0.7599	−0.0183	−0.0196
0.2203	−0.0196	−0.0194	0.8205	−0.0132	−0.0169
0.2797	−0.0213	−0.0212	0.8732	−0.0108	−0.0139
0.3393	−0.0224	−0.0227	0.9259	−0.0067	−0.0096
		2-(2-Methoxyethoxy)ethanol (1) + water (2)			
0.0435	−0.0118	−0.0114	0.2342	−0.0186	−0.0167
0.0495	−0.0125	−0.0120	0.2830	−0.0192	−0.0169
0.0618	−0.0135	−0.0129	0.3367	−0.0198	−0.0171
0.0705	−0.0141	−0.0134	0.4449	−0.0194	−0.0167
0.0817	−0.0146	−0.0139	0.5842	−0.0182	−0.0147
0.1063	−0.0156	−0.0147	0.6670	−0.0169	−0.0128
0.1226	−0.0162	−0.0152	0,7491	−0.0138	−0.0102
0.1460	−0.0168	−0.0156	0.8389	−0.0134	−0.0070
0.1791	−0.0175	−0.0161	0.9582	−0.0071	−0.0022
		2-(2-Ethoxyethoxy)ethanol (1) + water(2)			
0.0430	−0.0135	−0.0132	0.1913	−0.0179	−0.0172
0.0521	−0.0142	−0.0139	0.2485	−0.0184	−0.0176
0.0653	−0.0150	−0.0146	0.3116	−0.0190	−0.0178
0.0805	−0.0156	−0.0152	0.3975	−0.0186	−0.0175
0.1008	−0.0162	−0.0158	0.5108	−0.0172	−0.0163
0.1210	−0.0168	−0.0162	0.6172	−0.0152	−0.0143
0.1354	−0.0171	−0.0165	0.7235	−0.0132	−0.0115
0.1531	−0.0173	−0.0168	0.7818	−0.0116	−0.0098
0.1695	−0.0175	−0.0170	0.8860	−0.0046	−0.0062
		2-(2-Butoxyethoxy)ethanol (1) + water (2)			
0.0016	−0.0035	−0.0037	0.0778	−0.0160	−0.0158
0.0020	−0.0040	−0.0040	0.1025	−0.0166	−0.0163
0.0057	−0.0067	−0.0065	0.1352	−0.0172	−0.0168
0.0091	−0.0084	−0.0081	0.1713	−0.0175	−0.0171
0.0107	−0.0088	−0.0087	0.2244	−0.0178	−0.0173
0.0144	−0.0100	−0.0099	0.2695	−0.0181	−0.0174
0.0168	−0.0106	−0.0105	0.3081	−0.0180	−0.0173
0.0191	−0.0111	−0.0111	0,4136	−0.0172	−0.0166
0.0209	−0.0116	−0.0115	0.4994	−0.0160	−0.0154
0.0232	−0.0119	−0.0119	0.5582	−0.0140	−0.0143
0.0340	−0.0135	−0.0134	0.6696	−0.0119	−0.0115
0.0398	−0.0141	−0.0139	0.7403	−0.0105	−0.0095
0.0408	−0.0143	−0.0140	0.8806	−0.0043	−0.0050
0.0477	−0.0147	−0.0145	0.9321	−0.0035	−0.0028
0.0588	−0.0154	−0.0151			
		2-{2-(2-Methoxyethoxy)ethoxy}ethanol (1) + water (2)			
0.0010	0.0317	0.0316	0.2890	−0.0168	−0.0162
0.0025	0.0193	0.0198	0.3191	−0.0167	−0.0160
0.0040	0.0123	0.0123	0.3583	−0.0166	−0.0157
0.0082	0.0011	0.0010	0.4019	−0.0157	−0.0153
0.0147	−0.0064	−0.0062	0.4415	−0.0156	−0.0148
0.0380	−0.0131	−0.0129	0.4719	−0.0153	−0.0144

(*continued*)

TABLE IV Continued

x_1	$V_f^E \times 10^6$ (m^3 mol^{-1})		x_1	$V_f^E \times 10^6$ (m^3 mol^{-1})	
	Eqs. (6) and (18)	*Eq. (19)*		*Eqs. (6) and (18)*	*Eq. (19)*
0.0514	−0.0143	−0.0141	0.5187	−0.0132	−0.0123
0.0609	−0.0147	−0.0146	0.5754	−0.0131	−0.0122
0.0711	−0.0152	−0.0150	0.5898	−0.0112	−0.0120
0.0854	−0.0156	−0.0154	0.6561	−0.0102	−0.0104
0.1098	−0.0161	−0.0158	0.7082	−0.0091	−0.0090
0.1217	−0.0163	−0.0160	0.7359	−0.0081	−0.0083
0.1415	−0.0165	−0.0162	0.7820	−0.0072	−0.0070
0.1640	−0.0167	−0.0163	0.8142	−0.0058	−0.0061
0.1852	−0.0168	−0.0163	0.8802	−0.0037	−0.0042
0.2063	−0.0169	−0.0164	0.9349	−0.0026	−0.0025
0.2565	−0.0170	−0.0163	0.9739	−0.0010	−0.0010
	2-{2-(-Ethoxyethoxy)ethoxy}ethanol (1) + water (2)				
0.0004	0.0355	0.0362	0.2463	−0.0183	−0.0169
0.0016	0.0233	0.0230	0.2778	−0.0182	−0.0168
0.0021	0.0187	0.0191	0.3085	−0.0183	−0.0167
0.0041	0.0081	0.0085	0.3551	−0.0180	−0.0163
0.0066	0.0012	0.0012	0.4041	−0.0178	−0.0158
0.0099	−0.0042	−0.0040	0.4405	−0.0168	−0.0154
0.0144	−0.0082	−0.0079	0.4693	−0.0163	−0.0149
0.0215	−0.0112	−0.0110	0.5172	−0.0160	−0.0140
0.0337	−0.0136	−0.0134	0.5556	−0.0152	−0.0132
0.0418	−0.0146	−0.0143	0.6038	−0.0141	−0.0121
0.0525	−0.0153	−0.0149	0.6420	−0.0135	−0.0111
0.0613	−0.0158	−0.0154	0.6811	−0.0122	−0.0101
0.0714	−0.0162	−0.0157	0.7486	−0.0120	−0.0083
0.0827	−0.0166	−0.0160	0.7756	−0.0079	−0.0076
0.0914	−0.0168	−0.0162	0.8113	−0.0094	−0.0067
0.1127	−0.0172	−0.0165	0.8352	−0.0103	−0.0061
0.1437.	−0.0175	−0.0168	0.8804	−0.0055	−0.0048
0.1746	−0.0179	−0.0169	0.9549	0.0018	−0.0020
0.2059	−0.0181	−0.0169	0.9740	−0.0012	−0.0010
	2-{2-(2-Butoxyethoxy)ethoxy) ethanol (1) + water (2)				
0.0045	−0.0005	−0.0006	0.3062	−0.0167	−0.0159
0.0099	−0.0076	−0.0076	0.3418	−0.0163	−0.0155
0.0134	−0.0100	−0.0098	0.4033	−0.0153	−0.0148
0.0177	−0.0118	−0.0115	0.4651	−0.0143	−0.0138
0.0207	−0.0125	−0.0124	0.4965	−0.0134	−0.0133
0.0247	−0.0135	−0.0132	0.5465	−0.0131	−0.0123
0.0316	−0.0143	−0.0142	0.5766	−0.0125	−0.0117
0.0432	−0.0154	−0.0152	0.6303	−0.0118	−0.0104
0.0573	−0.0159	−0.0158	0.6961	−0.0102	−0.0089
0.0684	−0.0163	−0.0161	0.7515	−0.0075	−0.0075
0.0839	−0.0167	−0.0163	0.7845	−0.0085	−0.0068
0.1079	−0.0168	−0.0165	0.8367	−0.0042	−0.0055
0.1420	−0.0170	−0.0166	0.8824	−0.0056	−0.0043
0.1845	−0.0170	−0.0166	0.9209	−0.0022	−0.0031
0.2152	−0.0170	−0.0165	0.9518	−0.0013	−0.0019
0.2686	−0.0167	−0.0162	0.9713	−0.0008	−0.0011

molecules appear to occupy a void space in a more structured water lattice providing an ordered compact structure, thereby giving rise to a marked change in their properties in the water-rich region. Hence molecules become more ordered and hence more structured in an aqueous environment.

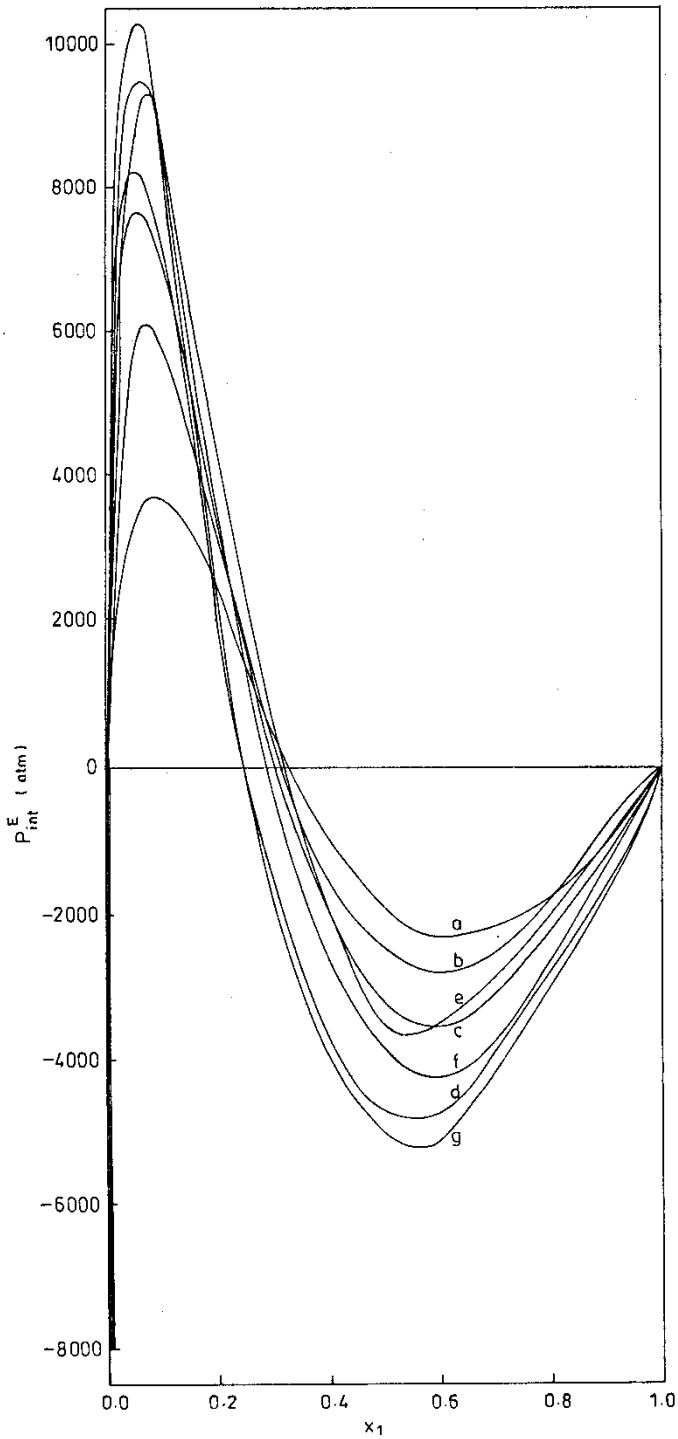

FIGURE 1 Excess internal pressure P^E_{int} for 2-methoxyethanol (a) +; 2-(2-methoxyethoxy)ethanol (b) +; 2-(2-ethoxyethoxy)ethanol (c) +; 2-(2-butoxyethoxy)ethanol (d) +; 2-{2-(2-methoxyethoxy)ethoxy}ethanol (e) +; 2-{2-(2-ethoxyethoxy)ethoxy}ethanol (f)+; 2-{2-(2-butoxyethoxy)ethoxy}ethanol (g) + water at 298.15 K.

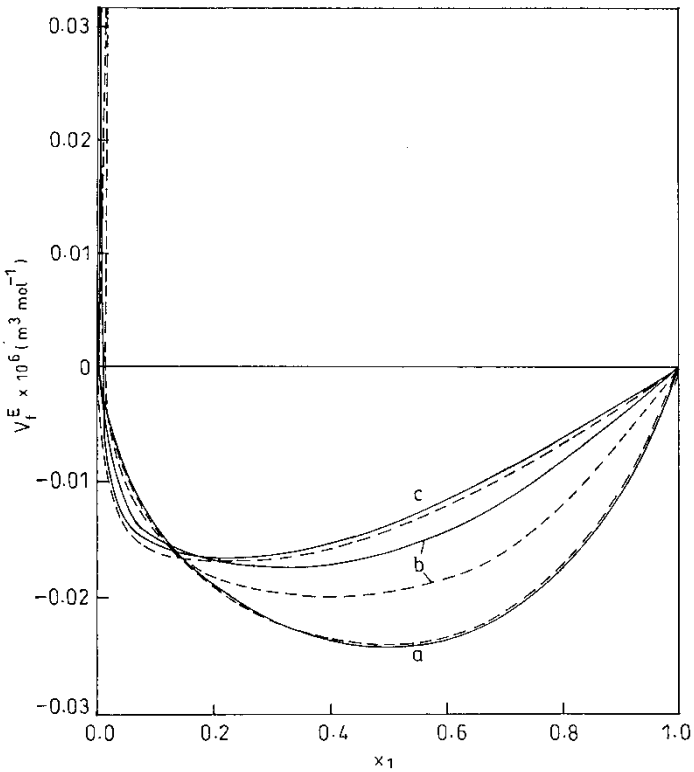

FIGURE 2 Excess free volume V_f^E for 2-methoxyethanol (a) +; 2-(2-methoxyethoxy)ethanol (b) +; 2-{2-(2-methoxyethoxy)ethoxy}ethanol (c) + water at 298.15 K. (- - - - -) drawn from Eq. (18) and (—) drawn from Eq. (19).

The values of P_{int}^E are negative at high concentrations of amphiphile for all the systems. Negative values of P_{int}^E mean that the mixture P_{int} is more cohesion than the corresponding ideal mixture $(P_{\text{int}})_{\text{id}}$, suggesting that, 'nonchemical interactions', is less than the 'chemical interactions' in the binary mixtures [10]. This is maximum at the intermediate range. As the concentration of ether in the mixture increases, the liquid is becoming less structured leading to specific interactions between unlike molecules and hence molecules acquiring their random configuration. Hence, a considerable structural enhancement takes place with the addition of ethers to water. Thus, we conclude that there is a increase in strength of interaction as the polar group as well as the alkyl chain length of the amphiphile increases.

Again, the square root of ced refers as the solubility parameter [12]. In comparison with the ced data of the pure components (Table I) it reveals that the interaction between unlike molecules enhances the miscibility of the two components. That is, the liquid water becomes increasingly miscible with the amphiphile. Cohesion falls with increasing the chain length and the oxyethylene group, resulting δ of amphiphiles moving away to water. On the other hand, the miscibility of the lower amphiphile with water rises (Table III) as the alkyl chain length and the polar head group of the amphiphile is increased. Intermolecular interactions rises on transfer to the higher amphiphile components; and cohesion also rises; δ of amphiphile + water mixtures become less like δ of water itself.

A perusal of Table IV shows that the excess free volume calculated from Eqs. (5) and (18) and those from Eq. (19) are in good agreement for all the systems investigated except with 2-(2-methoxyethoxy)ethanol and 2-{2-(2-ethoxyethoxy}ethoxy)ethanol. Small deviations between the two sets of values (Fig. 2) may be attributed to the uncertainties in the experimental data of α, κ_T, ρ, u, and η. The excess free volume decreases for all the systems when the mixtures are created. The effect is, that at intermediate x_1, the molecules of the two components can accommodate easily due to dissimilar molecular size, break of the water structure, or both. The free volume and excess free volume behavior of water + amphiphile systems are also consistent [31] with excess molar isentropic compressibilities $K_{s,m}^E$ and deviations of the speeds of sound u^D.

Acknowledgment

Harsh Kumar thanks the Council of Scientific and Industrial Research (CSIR), New Delhi for a Senior Research Fellowship (Fellowship no. 9/105/107/2001/EMR-1) and financial assistance.

References

[1] G. Douheret, P. Lajoie, M.I. Davis, J.L. Ratliff, J. Ulloa and H. Hoiland (1995). *J. Chem. Soc. Faraday Trans.*, **91**, 2291.
[2] A. Pal and R.K. Bhardwaj (2002). *J. Chem. Thermodyn.*, **34**, 1157.
[3] A. Pal and H. Kumar (2001). *J. Mol. Liquids.*, **94**, 163.
[4] G. Douheret and A. Pal (1988). *J. Chem. Engg. Data*, **42**, 689.
[5] G. Douheret, S. Salgado, M.I. Davis and J. Loya (1992). *Thermochim. Acta*, **207**, 313.
[6] G. Douheret, A. Pal and M.I. Davis (1990). *J. Chem. Thermodyn.*, **22**, 99.
[7] A. Pal and Y.P. Singh (1996). *Indian J. Chem.*, **35A**, 1120; **35A**, 137.
[8] A. Pal and Y.P. Singh (1997). *J. Chem. Engg. Data*, **42**, 689.
[9] A.F.M. Barton (1971). *J. Chem. Educ.*, **48**, 156.
[10] M.R.J. Dack (1975). *Aust. J. Chem.*, **28**, 1643.
[11] M.R.J. Dack (1975). *Chem. Soc. Rev.*, **4**, 211.
[12] J.H. Hildebrand and R.L. Scott (1964). *Solubility of Non-electrolytes*, 3rd Edn. Reinheld, New York.
[13] C.V. Suryanarayana (1989). *Indian J. Pure Appl. Phys.*, **28**, 757.
[14] J.D. Pandey, N. Dubey, D.K. Dwivedi and R. Dey (2001). *Phys. Chem. Liq.*, **39**, 781.
[15] J.A.R. Renuncio, G.J.F. Breedveld and J.M. Prausnitz (1977). *J. Phys. Chem.*, **81**, 324.
[16] C.V. Suryanarayana (1986). *Indian J. Chem.*, **25A**, 538.
[17] R. Sabesan, R. Varadarajan and M. Natarajan (1988). *Indian J. Pure Appl. Phys.*, **26**, 504.
[18] R. Mishra (1979). *Acoust. Lett.*, **3**, 60.
[19] J.H. Hildebrand, J.M. Prausnitz and R.L. Scott (1970). *Regular and Related Solutions.* Van Nostrand-Reinheld, Princeton, N.J.
[20] H.S. Frank and M.W. Evans (1945). *J. Chem. Phys.*, **13**, 507.
[21] C.V. Suryanarayana and J. Kuppusami (1976). *J. Acoust. Soc. India*, **4**, 75.
[22] A. Dhanalakshmi (1980). *J. Acoust. Soc. India*, **8**, 29.
[23] J.F. Kincaid and H. Eyring (1938). *J. Chem. Phys.*, **6**, 620.
[24] S. Glasstone (1973). *Theoretical Chemistry*, p. 468. Affiliated East-west Press, New Delhi.
[25] J.O. Hirschfelder, D.P. Stevenson and H. Eyring (1937). *J. Phys. Chem.*, **5**, 896.
[26] C.V. Suryanarayana, P. Aruna and S. Natarajan (1991). *Ind. J. Tech.*, 327.
[27] C.V. Suryanarayana and J. Kuppusami (1983). *J. Acoust. Soc. India*, **11**, 13.
[28] G.S. Kell (1967), *J. Chem. Engg. Data*, **12**, 66.
[29] J.A. Riddick, W.B. Bunger and T.K. Sakano (1986). *Techniques of Chemistry*, 4th Edn., Vol. 2. Wiley-Interscience, New York.
[30] V.A. Del Grosso and C.W. Madar (1972). *J. Acoust. Soc. Amer.*, **52**, 1442.
[31] G.S. Kell (1975). *J. Chem. Engg. Data*, **20**, 97.
[32] B. Das and D.K. Hazra (1993). *J. Chem. Engg. Data*, **38**, 361.
[33] G. Roux, G. Perron and J.E. Desnoyers (1978). *J. Solution. Chem.*, **7**, 639.
[34] A. Pal and Y.P. Singh (1996). *J. Chem. Thermodyn.*, **28**, 143.

[35] G. Douheret, M.I. Davis, J. Ulloa, H. Hoiland and J. Fjellanger (1996). *J. Chem. Soc. Faraday Trans.*, **92**, 2369.
[36] Y.P. Singh (1996). *Ph.D. Doctoral Thesis*. Kurukshetra University, Kuruksheta, India.
[37] A. Pal and Y.P. Singh (1994). *J. Chem. Thermodyn.*, **26**, 1063.
[38] A. Pal and Y.P. Singh (1995). *J. Chem. Therrnodyn.*, **27**, 1329.