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Microheterogeneity in Aqueous-Organic Solutions: Heat Capacities, Volumes and Expansibilities of Some Alcohols, Aminoalcohol and Tertiary Amines in Water

Geneviève Roux,[1] David Roberts,[2] Gérald Perron,[2] and Jacques E. Desnoyers[2,3]

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The heat capacities per unit volume and the densities of aqueous solutions of 2-propanol, neopentanol, tert-amylalcohol, 2-amino-2-methylpropanol, triethylamine and diethylmethylamine were measured, in many cases as a function of temperature, over the whole mole fraction or solubility range. Apparent and partial molal heat capacities, volumes and expansibilities were derived. The concentration dependence of these functions suggest the existence of transitions in some of these systems, in the water-rich region, qualitatively similar to micellization. The large relaxation contribution observed with some of the thermodynamic functions of hydrophobic alcohols and amines suggests a reinforcement of hydrophobic hydration due to strong hydrogen-bonding interactions of the polar groups with water.

KEY WORDS: Heat capacity; density; expansibility; volume; aqueous solutions; 2-propanol; neopentanol; t-amylalcohol

1. INTRODUCTION

The systematic studies carried out in this laboratory of the thermodynamic properties of nonelectrolytes in water have suggested the existence of transitions in aqueous solutions of certain organic molecules. The heat capacity was the principal property investigated for this purpose, since its magnitude is very sensitive to structural changes in solution. The concentration dependence of the apparent or partial molal heat capacity, ϕ_C or $\overline{C}_{p,2}$, changes according to the nature of the

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[1] Laboratoire de Thermodynamique et de Cinétique Chimique, Université de Clermont-Ferrand 2, 63170 Aubière, France.

[2] Dept of Chemistry, Université de Sherbrooke, Sherbrooke, Que. Canada, J1K 2R1.

[3] To whom correspondence should be addressed.

solute. With aqueous solutions of many liquids, such as dimethylformamide,(1) acetamide,(2) dimethylsulfoxide,(2) ketones,(2,3) ethers,(3,4) esters(3) and the lower alkoxyethanols (methyl, ethyl),(5) ϕ_C decreases monotonically from the value at infinite dilution to that of the pure liquid or to the value at the solubility limit. However, with some hydrophobic solutes such as *tert*-butanol,(6) (*t*-BuOH), 2-*n*-butoxyethanol(5) and piperidine,(4) ϕ_C passes through a maximum in the water-rich region and then decreases rapidly to the value of the pure organic liquid. The dramatic change in ϕ_C can be compared to that associated with micellization in the case of surfactants(7) and is supporting evidence for microheterogeneity in the binary systems.(8,9)

Alcohols are major components of microemulsions.(10) There could therefore be a relationship between the action of the alcohol in stabilizing the microemulsion and the microheterogeneity of its aqueous solution. Therefore, other solutes which show microheterogeneity in water should also be good cosurfactants for the formation of microemulsions; 2-*n*-butoxyethanol was investigated in this respect(11) and was shown to solubilize large quantities of decane even without the addition of surfactants or electrolytes.

Several possible factors can contribute to the microheterogeneity of these solutions, such as the hydrophobic character of the molecule, the tendency for the system to unmix, the geometry of the molecule and the nature of the polar group. In the present study, we will further this investigation by examining other alcohols which are of potential use as cosurfactants in microemulsions, i.e. 2-propanol (2-PrOH) *tert*-amylalcohol (*t*-PeOH), neopentanol (*neo*-PeOH). Branched alcohols were preferred to normal ones in view of their higher solubility in water. We will also examine tertiary amines which have a lower critical solution temperature, i.e. triethylamine (Et_3N) and diethylmethylamine ($MeEt_2N$), and one aminoalcohol, i.e. 2-amino-2-methyl-propanol (AMePrOH). Concurrent studies are also in progress on the ternary systems 2-PrOH-H_2O-Benzene, $MeEt_2N$-H_2O-Benzene and $MeEt_2N$-H_2O-Decane.

Heat capacities measured by flow microcalorimetry require the simultaneous determination of the densities. Apparent and partial molal volumes, ϕ_V and $\overline{V}_2$, can therefore be measured along with the heat capacities, and corresponding expansibilities, ϕ_E and $\overline{E}_2$, can be derived from the temperature dependence of the volumes.

2. EXPERIMENTAL

Pure (99%) neopentanol (Aldrich Chemicals) was used without further purification. The water content of the solid product was determined by Karl Fischer titration and the molalities of the solutions were corrected accordingly. The limit of miscibility at 25°C was found to be approximately 0.35 mol-kg^{-1}. The *t*-PeOH (J. T. Baker Chemical Co.) was dried over molecular sieves. The maximum solution concentration was 1.17 m at 25°C. AMePrOH (Aldrich Chemicals) was used without further purification and the solutions were made up using 0.07 m NaOH as solvent. 2-PrOH (Fisher Scientific, ACS Certified) was distilled from CaO and stored over molecular sieves. Et_3N (Baker) and $MeEt_2N$ (Digni Corp. and Pfaff and Bauer) were distilled and the central fractions were stored in a refrigerator in the dark over 4×10^{-8} cm molecular sieves. Their purity (99%) was verified by vapor-phase chromatography (carbowax, 10%). Their solutions were prepared as soon as possible after purification with 0.06 m NaOH. All solutions were prepared by weight. The water used was distilled and deionized.

The procedure used for density and heat capacity measurements is the same as in our previous studies(1-7) and need not be described. However, in the case of AMePrOH, the viscosity of the more concentrated solution became too large for the flow microcalorimeter. Above 0.15 mole fraction the specific heats were measured with a Parr solution calorimeter. Solution homogeneity and temperature monitoring could be maintained successfully up to solute mole fractions of 0.8. At these high concentrations the precision on the difference in specific heat obtained with the solution calorimeter is of the order of 1% which is acceptable. A few points were also obtained with this system using a flow Picker mixing microcalorimeter(12) which has much larger tubes.

In some of the measurements the densimeter and flow microcalorimeter were placed in series. As a consequence the temperature of the density measurements were then 0.35°K lower than that of the heat capacity measurements. This difference in temperature on the densities makes a negligible error on the calculation of ϕ_C.

3. RESULTS

The apparent molal volumes and heat capacities were calculated in the usual way(1-7) from the differences in densities and in specific heat capacities. Measurements were made over the whole mole

Table I. Densities and Heat Capacities of Water

T/°C	d_0 [a]	$c_{p0} = \sigma_0/d_0$ [b]
5	0.999964	4.2019
10	0.999700	4.1919
15	0.999101	4.1855
25	0.997047	4.1793
40	0.992219	4.1783

[a] gm cm^{-3}. [b] JK^{-1}-mol^{-1}.

fraction or solubility range. Neopentanol and AMePrOH were measured at 25°C only, *t*-PeOH and 2-PrOH at 10 and 25°C, Et_3N at 5, 15 and 25°C and $MeEt_3N$ at 10, 25 and 40°C. The experimental data for water are given in Table I and for the solutions in Table II.

Here, m and x_2 are the molalities and mole fractions, respectively, of the organic solutes, d is the density in g-cm^{-3} and $10^{-3}\Delta\sigma/\sigma_o$ is the relative change in the heat capacity per unit volume.

The low concentration data can be fitted with the equation

$$\phi_Y = \phi_Y^o + A_Y m \qquad (1)$$

where $\phi_Y^o = \overline{Y}_2^o$, the infinite dilution value, Y stands for V, C_p or E and m is the molality of the solute. The parameters ϕ_Y^o and A_Y and the molar value Y^o of the pure liquids are given in Tables III-V and compared with available literature values. In general the agreement is excellent, the largest differences being of the order of 0.5 cm^3-mol^{-1}. The agreement is not quite so satisfactory with heat capacities, but in the cases where the disagreement is significant, the literature data were extrapolated from relatively high concentrations. The most severe test comes from the direct comparison of ϕ_V and ϕ_C of 2-PrOH with those of other authors at 25°C. Brunn and Hvidt(13) made a thorough investigation of ϕ_V and Roux *et al.*(15) have independently measured ϕ_V and ϕ_C. As it will be shown later, their data essentially coincide with ours within the respective uncertainties. We are therefore confident that our accuracy for ϕ_V and ϕ_C is of the order of 0.5 cm^3-mol^{-1} and 5 JK^{-1}-mol^{-1}. Our precision for ϕ_V and ϕ_C is about an order of magnitude better. It should be noted that the data for the three amine salts were obtained in a slightly alkaline solution (0.06 to 0.07 m). This concentration of NaOH is sufficient to suppress any hydrolysis and should have little effect on the actual values of ϕ_V.(4,17,22)

Table II. Densities and Heat Capacities per unit Volume of Some Alcohols, Amines and Aminoalcohol in Water

m	X_2	$10^3\Delta d$	ϕ_V cm^3mol^{-1}	$\Delta\sigma/\sigma_0$	ϕ_C $JK^{-1}mol^{-1}$
		2-PROPANOL 25°C			
0.2850	0.0051	- 3.1151	71.495	4.3632	363.19
0.6718	0.0119	- 6.8464	71.017	10.422	363.84
0.7615	0.0135	- 7.7056	71.006	11.822	364.27
0.9542	0.0169	- 9.3250	70.771	14.807	364.12
1.5833	0.0277	- 14.243	70.332	24.997	366.38
1.9991	0.0347	- 17.083	70.075	31.179	366.29
2.4098	0.0416	- 19.779	69.922	37.168	366.65
3.3162	0.0563	- 25.168	69.671	46.758	362.82
4.9523	0.0818	- 35.238	69.906	44.184	341.45
7.5401	0.1195	- 50.734	70.641	- 3.172	291.67
10.2993	0.1564	- 67.223	71.076	- 5.879	257.25
20.4664	0.2692	-100.06	73.287	- 0.1905	208.30
61.143	0.5239	-161.79	75.131	- 0.3598	175.83
172.51	0.7564	-192.50	76.091	- 0.4442	165.47
		2-PROPANOL 10°C			
0.3757	0.007	- 0.4050	71.193	0.7090	379.57
0.7694	0.014	- 0.7549	70.468	1.4193	376.82
1.0820	0.019	- 1.0041	70.108	1.9625	375.60
1.3485	0.024	- 1.1943	69.814	2.4185	374.82
2.0944	0.036	- 1.6373	69.072	3.5471	370.72
2.4667	0.043	- 1.8270	68.786	4.0485	368.73
3.5511	0.060	- 2.3128	68.213	5.2915	363.45
4.2849	0.072	- 2.6353	68.066	5.7257	357.59
5.1724	0.085	- 3.0560	68.112	5.3727	344.31
8.3810	0.131	- 4.8178	69.205	- 1.5668	277.63
10.9013	0.164	- 6.150	70.074	- 7.3536	243.78
20.8551	0.273	- 9.682	71.709	-21.148	194.45
57.0724	0.507	- 14.91	73.725	-38.156	163.05
578.41	0.912	- 19.80	75.390	-52.398	146.59
		t-AMYL ALCOHOL 10°C			
0.07668	0.0014	- 0.9368	100.495	2.6312	566.09
0.11355	0.0020	- 1.3890	100.556	3.8932	566.76
0.14275	0.0026	- 1.7048	100.297	4.9076	566.49
0.1795	0.0032	- 2.1129	100.166	6.1237	565.34
0.3350	0.0060	- 3.7229	99.667	11.449	565.72
0.4849	0.0087	- 5.1407	99.295	16.754	567.92
0.6361	0.0113	- 6.4297	98.927	22.161	569.80
0.7851	0.0139	- 7.5007	98.475	27.245	569.39
0.8705	0.0154	- 8.1466	98.342	30.514	571.64
0.9378	0.0166	- 8.6670	98.276	33.369	574.74
1.0311	0.0182	- 9.2944	98.108	37.202	577.67
1.1670	0.0206	- 10.183	97.905	42.234	579.32
		t-AMYL ALCOHOL 25°C			
0.0957	0.0017	- 1.1900	101.040	2.6773	539.08
0.2057	0.0037	- 2.4803	100.794	6.0007	544.47
0.2119	0.0038	- 2.5204	100.633	6.1996	544.24
0.3297	0.0059	- 3.8468	100.535	9.6601	545.42
0.3468	0.0062	- 3.9861	100.376	10.219	545.71
0.3966	0.0071	- 4.5582	100.431	11.687	546.52
0.4854	0.0087	- 5.4345	100.221	14.231	546.10
0.5832	0.0104	- 6.4131	100.117	17.835	552.42
0.6164	0.0110	- 6.6360	99.905	18.650	550.51
0.7338	0.0130	- 7.7117	99.754	22.390	552.50
0.8511	0.0151	- 8.8356	99.738	26.901	558.88
0.9157	0.0162	- 9.2683	99.518	29.345	560.80
0.9931	0.0176	- 10.076	99.624	32.473	565.26
1.0761	0.0190	- 10.874	99.663	35.897	569.62
1.1744	0.0207	- 11.590	99.495	39.582	571.86
	1.0	-193.05	109.640		
		NEOPENTANOL 25°C			
0.0499	0.00090	- 0.6805	102.173	0.9338	504.21
0.0526	0.00095	- 0.7180	102.226	0.9832	505.57
0.0941	0.00169	- 1.2793	102.230	1.7584	504.86
0.1181	0.00212	- 1.5868	102.093	2.1946	504.03
0.1456	0.00262	- 1.9383	101.998	2.7394	504.80
0.1695	0.00304	- 2.2457	101.972	3.2234	505.78
0.1966	0.00353	- 2.5976	101.968	3.7541	506.29
0.2208	0.00396	- 2.8881	101.864	4.2245	506.22
0.2627	0.00471	- 3.4284	101.891	4.9594	505.59
0.2790	0.00500	- 3.6251	101.850	5.2976	506.00
0.3145	0.00563	- 4.0018	101.619	5.8157	503.19
0.3441	0.00616	- 4.4129	101.762	6.2828	503.01
		2-AMINO-2-METHYL-PROPANOL 25°C			
0.1008	0.0018	- 0.2394	91.523	- 0.4271	363.96
0.2535	0.0045	- 0.5213	91.229	- 1.0260	363.30
0.4333	0.0077	- 0.8299	91.116	- 1.6865	363.23
0.6674	0.0119	- 1.1655	90.978	- 2.5188	362.83
0.9972	0.0176	- 1.4639	90.726	- 3.5948	362.08
1.1656	0.0206	- 1.5496	90.595	- 4.1652	361.45
1.7046	0.0298	- 1.6845	90.266	- 5.6079	360.73
1.9500	0.0339	- 1.6910	90.145	- 6.3100	360.19
2.2082	0.0383	- 1.6546	90.024	- 7.2479	359.14
2.6039	0.0448	- 1.5879	89.878	- 8.5244	358.09
2.8104	0.0482	- 1.5631	89.822	- 9.3109	357.40
3.1066	0.0530	- 1.4861	89.737	- 10.7924	355.82
3.9892	0.0670	- 1.3536	89.586	- 16.0617	350.93
4.1634	0.0698	- 1.3428	89.568	- 17.4214	349.69
5.1913	0.0855	- 1.4604	89.538	- 26.8119	341.96
6.6861	0.1075	- 2.1697	89.645	- 45.22	328.85
8.2214	0.1290	- 3.4897	89.864	- 70.33	312.84
8.7431	0.1361	- 4.0361	89.950	- 77.93	308.82
10.0991	0.1539	- 5.6481	90.194	- 96.60	300.02
10.6107^a	0.1605	---	---	---	295.37
11.3066	0.1692	- 7.1349	90.401	-116.00	290.59
16.7932	0.2323	-14.283	91.280	---	---
23.1464	0.2942	-21.527	92.036	---	---
27.6197^a	0.3322	---	---	---	254.83
38.1272	0.4072	-32.824	93.040	---	---
40.8919^a	0.4242	---	---	---	245.69
64.2204^a	0.5364	---	---	---	238.43
71.9026	0.5643	-45.658	94.054	---	---
124.1066	0.6910	-54.282	94.703	---	---
143.4846^a	0.7210	---	---	---	236.27
196.3466	0.7796	-59.367	95.071	---	---
242.756^a	0.8139	---	---	---	231.21
811.444	0.9360	-67.393	95.654	---	---
		DIETHYLMETHYLAMINE 10°C			
0.0692	0.00125	- 1.351	106.47	1.59	547.81
0.1250	0.00225	- 2.391	106.20	2.79	538.53
0.1572	0.00283	- 2.968	106.00	3.57	539.60
0.2335	0.00479	- 4.285	105.62	5.22	537.22
0.3060	0.00548	- 5.456	105.32	6.88	536.93
0.3948	0.00706	- 6.877	104.96	9.01	538.09
0.5700	0.01016	- 9.395	104.28	13.27	539.06
0.8306	0.01474	- 12.834	103.58	20.47	544.88
1.0843	0.01916	- 15.839	103.07	29.20	555.99
1.3483	0.02371	- 18.803	102.71	40.61	572.64
1.5286	0.02680	- 20.794	102.57	49.56	585.40
1.7973	0.03136	- 23.913	102.60	61.77	598.92
2.165	0.03753	- 28.443	102.90	69.38	594.81
2.520	0.04343	- 33.026	103.36	66.76	571.62
3.174	0.05312	- 40.819	104.19	47.67	520.40
4.635	0.07706	- 59.334	105.92	- 15.75	421.83
10.135	0.1544	-103.66	108.28	-169.57	306.30
23.167	0.2945	-159.20	111.44	-337.0	252.23
58.099	0.5114	-211.53	114.74	-460.4	225.90
320.87	0.8525	-258.31	118.15	-572.09	204.02
b	1	-272.13	119.29	-611.60	193.78
		DIETHYLMETHYLAMINE 25°C			
0.0611	0.00110	- 1.204	107.03	1.11	521.34
0.0942	0.00169	- 1.841	106.93	1.73	522.43
0.1432	0.00257	- 2.762	106.77	2.61	521.39
0.1613	0.00290	- 3.083	106.63	2.97	521.85
0.2522	0.00452	- 4.709	106.36	4.71	522.57
0.3225	0.00578	- 5.926	106.19	6.15	524.17
0.4400	0.00786	- 7.893	105.96	8.58	526.05
0.5494	0.00980	- 9.672	105.79	11.36	531.40
0.7181	0.01277	- 12.295	105.58	15.51	536.19
0.8535	0.01514	- 14.301	105.43	19.33	541.57
1.0176	0.01800	- 16.678	105.31	24.73	550.32
1.3324	0.02344	- 21.362	105.45	36.12	567.60
1.5721	0.02754	- 24.821	105.57	41.88	568.71
1.8550	0.03234	- 29.137	105.96	43.51	557.85
2.1343	0.03703	- 33.453	106.40	40.54	539.87
2.3899	0.04128	- 37.328	106.77	35.77	522.59
3.0746^b	0.05248	- 45.627	107.25	16.91	477.47
6.599	0.1063	- 89.166	110.53	- 92.5	359.20
13.045	0.1903	-132.375	112.57	-218.0	297.00
14.557	0.2076	-142.07	112.97	-234.5	292.9
23.915	0.3011	-178.08	115.11	-350.5	250.2
32.370^b	0.3683	-193.43	115.92	-391.5	243.4
48.707^b	0.4674	-217.12	117.49	-443.6	234.3
112.465^b	0.6695	-252.19	120.04	-524.9	218.1
213.343^b	0.7935	-268.45	121.36	-560.5	211.3
	1	-290.46	123.35	-610.9	200.0

[a] Values obtained from Parr static calorimeter at 25°C. [b] Measurements made in water and not in a 0.06 N NaOH solution.

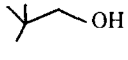
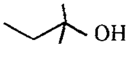
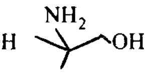
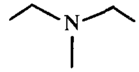
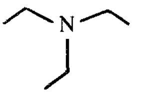
Table II. Continued

m	X_2	$10^3\Delta d$	ϕ_V cm^{3}mol^{-1}	$\Delta\sigma/\sigma_0$	ϕ_C JK^{-1}mol^{-1}
DIETHYLMETHYLAMINE 40°C					
0.0692	0.00125	- 1.405	108.24	1.03	510.89
0.1250	0.00225	- 2.507	108.12	1.86	510.77
0.1572	0.00283	- 3.126	108.01	2.34	510.53
0.2335	0.00419	- 4.560	107.81	3.52	511.04
0.2344	0.00420	- 4.510	107.53	3.59	510.86
0.3060	0.00548	- 5.894	107.68	4.82	513.91
0.3948	0.00706	- 7.535	107.68	6.37	516.17
0.5700	0.01016	- 10.591	107.50	9.46	518.71
0.6186	0.01102	- 11.090	106.90	10.19	516.02
0.8306	0.01474	- 14.948	107.38	14.78	525.57
0.9243	0.01638	- 16.088	106.92	16.73	525.77
1.0843	0.01916	- 19.289	107.64	20.63	534.43
1.3237	0.02329	- 22.942	107.59	23.77	531.15
1.3483	0.02371	- 23.933	108.12	22.48	527.45
1.5286	0.02680	- 27.040	108.40	23.32	523.13
1.7370	0.03034	- 30.036	108.34	24.49	518.59
1.7973	0.03136	- 31.921	109.03	22.06	512.79
2.165	0.03753	- 38.479	109.79	20.23	503.00
2.3683	0.04092	- 40.899	109.55	17.99	493.71
2.520	0.04343	- 44.632	110.43	14.97	489.14
3.1143	0.05312	- 54.315	111.28	5.18	470.39
3.8170	0.06434	- 63.010	111.33	- 5.61	452.57
4.635	0.07706	- 75.769	112.68	- 22.83	435.71
10.135	0.1544	-128.12	115.19	-127.3	369.5
23.167	0.2945	0181.96	116.90	-276.5	300.7
58.099	0.5114	-233.81	119.81	-666.7	242.6
320.87	0.8525				
[b]	1	-302.17	125.80	-631.5	192.10
TRIETHYLAMINE 5°C					
0.097817	0.001759	- 1.805	119.35	3.06	632.2
0.21492	0.003857	- 3.744	118.56	6.08	617.9
0.30532	0.005470	- 5.071	117.91	8.92	620.4
0.37965	0.006793	- 6.184	117.72	11.55	625.9
0.50286	0.008978	- 7.819	117.17	15.76	629.5
0.60657	0.01081	- 9.116	116.80	19.7	634.6
0.68020	0.01211	- 9.985	116.55	23.4	643.4
0.78604	0.01396	- 11.192	116.25	29.0	655.4
0.87817	0.01557	- 12.208	116.03	35.0	669.6
0.95664	0.01694	- 13.090	115.92	41.2	685.5
1.1994	0.02113	- 15.923	115.84	68.0	755.1
1.3351	0.02349	- 17.638	115.97	81.0	778.6
1.6117	0.02822	- 21.591	116.63	93.3.	776.0
1.7066	0.02983	- 23.016	116.89	93.6	764.5
1.9427	0.03381	- 26.593	117.53	91.4	733.9
2.8819	0.04936	- 40.178	119.44	55.8	609.2
2.4003	0.04145	- 33.387	118.58	75.9	666.6
3.6167	0.06114	- 49.875	120.51	22.9	542.9
6.1202	0.09931	- 76.847	125.32	- 62.4	439.3
23.6375	0.29866	-160.718	128.08	-334.2	298.3
54.813	0.4968	-199.579	130.98	-477	251.3
[b]	1	-262.14	137.15	-645	204.4
TRIETHYLAMINE 15°C					
0.1290	0.00232	- 2.373	119.51	3.55	614.9
0.2162	0.00388	- 3.831	119.02	5.93	613.7
0.4152	0.00742	- 6.938	118.37	11.81	618.1
0.6018	0.01072	- 9.585	117.90	19.17	634.0
0.7808	0.01387	- 12.021	117.66	29.5	662.6
0.9815	0.01738	- 14.911	117.80	51.1	733.3
1.2355	0.02178	- 18.971	118.44	73.4	777.7
1.4505	0.02547	- 22.713	119.21	82.9	776.5
1.6893	0.02954	- 26.873	119.97	89.8	766.7
1.7672	0.03086	- 28.136	120.14	98.2	781.8
1.9492	0.03393	- 37.313	120.68		
2.9249	0.05006	- 46.955	122.64		
6.3677	0.1029	- 87.921	125.68		
15.0006	0.2128	-140.731	128.26		
331.263	0.8565	-252.547	135.92		
	1	-261.537	137.19	-616	219.8
TRIETHYLAMINE 25°C					
0.12904	0.00232	- 2.451	120.72	3.02	601.2
0.21618	0.00388	- 4.018	120.19	5.15	601.7
0.41524	0.00742	- 7.265	119.48	10.6	608.6
0.60181	0.01073	- 10.110	119.12	18.2	630.5
0.05031	0.000905	- 0.972	120.67	1.18	600.56
0.10879	0.001956	- 2.062	120.42	2.58	601.32
0.14583	0.00262	- 2.781	120.63	3.50	604.
0.19968	0.003584	- 3.697	120.18	4.85	603.95
0.27349	0.004903	- 4.968	119.98	6.79	606.2
0.33732	0.00604	- 6.014	119.77	8.40	606.44
0.39896	0.007136	- 7.028	119.68	10.58	613.82
[b]	1	-268.80	138.9_5		

[b] Measurements made in water and not in a 0.06 N NaOH solution.

It should be mentioned that the amines have a tendency to decompose at high temperature. An estimate of the importance of the decomposition on our measurements was obtained from two sets of data. In the first case, measurements were made at 40°C on a solution of $MeEt_2N$ previously used for the measurements at 10°C and stored at 4°C. Another set of measurements was obtained in the water-rich region at 40°C from a freshly prepared solution kept in the cold until used. It was found that the discrepancy in ϕ_C between both sets of data was of the order of the experimental uncertainty. However, in the case of volumes, the difference was of the order of 0.5 cm^3-mol^{-1}, the freshly prepared solution having the lower values.

Table III. Apparent Volumes of some Alcohols, Amines and Aminoalcohol in Water and Molar Volumes of the Pure Solutes

Solute		T °C	ϕ_V^o cm^3-mol^{-1}	A_V	m_{max}[a] mol-kg^{-1}	V_2^o cm^3-mol^{-1}
MeOH		25	38.25(14)			40.73(16)
EtOH		25	55.12(14)			58.68(16)
2-PrOH		9.65	71.74	- 1.55	1.05	75.62
		24.65	71.79	- 1.07	0.95	76.82
		25	71.91(15)			76.99(15)
		25	71.71(13)			76.96(15)
t-BuOH		25	87.76(6)	- 1.89	0.4	94.95(6)
neo-PeOH		24.65	102.32	- 2.01	0.2	
			101.87(14)			
t-PeOH		9.65	100.75	- 3.22	0.3	107.76(16)
		24.65	101.15	- 1.93	0.6	109.64
						109.58(16)
AMePrOH		24.65	91.41	- 0.67	1.0	95.85
MeEt$_2$N		10	106.84	- 5.29	0.3	119.29
		25	107.25	- 3.58	0.25	123.35
			106.77(17)			
			109.4(18)			
		40	108.43	- 2.66	0.25	125.80
Et$_3$N		5	120.03	- 6.93	0.35	137.15
		15[b]	119.94	- 3.85	0.4	137.19
		25	120.87	- 3.32	0.35	138.25
			120.9(17)			139.93(17)
			119.7(19)			

[a] Maximum molality of linear region. [b] Measured by C. de Visser.

Table IV. Heat Capacities of Some Alcohols, Amines and Aminoalcohol in Water and the Molar Heat Capacity of the Pure Solutes

Solute	T °C	ϕ^{o}_{C} JK^{-1}-mol^{-1}	A_C	m_{max}[a] mol-kg^{-1}	$C^{o}_{p,2}$ JK^{-1}-mol^{-1}
MeOH	25	158.2(14)			81.1(16)
EtOH	25	260.3(14)			111.9(16)
2-PrOH	10	381.1	-5.0	2.1	145.4
	25	362.3 375(20) 364(15) 385(21)	2.4	1.5	161.2 153.3(20) 155(15)
t-BuOH	25	463.6(6)	7.91	1.2	210(6)
neo-PeOH	25	503.6 503.5(14)	10.6	0.23	
t-PeOH	10	566.6	2.9	0.35	
	25	538.8 563.0(21)	19.9	0.65	250.3(21)
AMePrOH	25	364.0	-1.9	1.0	229.5
$MeEt_2N$	10	542.2	-19.0	0.3	194
	25	521.3 533.5(22) 515(23)	4.3	0.25	200
	40	510.7 519.6(22)	0.8	0.25	192
Et_3N	5	629.0	-10.0	0.35	200 214(24b)
	15	612.2[b]	13.4	0.45	220 220(24b)
	25	599.7 609(24a)	21.8	0.35	

[a] Maximum molality of linear region. [b] Measured by C. de Visser.

4. DISCUSSION

Most of the changes occurring in aqueous-organic mixtures are in the water-rich region. Molar excess functions, which are generally favored in a discussion of the properties of binary mixtures, tend to attenuate the changes at both ends of the mixture. Partial and apparent molal quantities do not suffer from this drawback and reflect more readily the characteristic interactions and structural changes in the water-rich region. This is especially so with systems that are not completely miscible with water.

Table V. Expansibility of some Alcohols and Amines in Water and the Molar Expansibility of the Solutes

Solute	T°C	$\phi_E^{\circ a}$	$E_2^{\circ a}$
2-PrOH	17.5	0.003	0.08
t-PeOH	17.5	0.027	
$MeEt_2N$	17.5	0.027	0.27
	25	0.053	0.22
	32.5	0.079	0.16
Et_3N	10	-0.009	0.004
	15	0.042	0.06
	20	0.093	0.11

[a] cm^3-K^{-1}-mol^{-1}.

4.1. Volumes

The concentration dependence of ϕ_V of $MeEt_2N$, AMePrOH and 2-PrOH is shown over the whole mole fraction range in Fig. 1. The partial molal value $\overline{V}_2$ can readily be calculated from $\overline{V}_2 = \phi_V + x_1x_2 d\phi_V/dx_2$ and is also shown in Fig. 1. These results are typical of most aqueous-organic mixtures; $\overline{V}_2^\circ$ is smaller than the molar volume V_2° and $\overline{V}_2$ or ϕ_V goes through a minimum in the water-rich region.(25)

The trends with the branched alcohols in the water-rich region are shown in more detail in Fig. 2. The larger the hydrophobic character (i.e. number of CH_2 groups) the more negative is the initial slope. It is rather obvious from this figure that the two pentanols fall

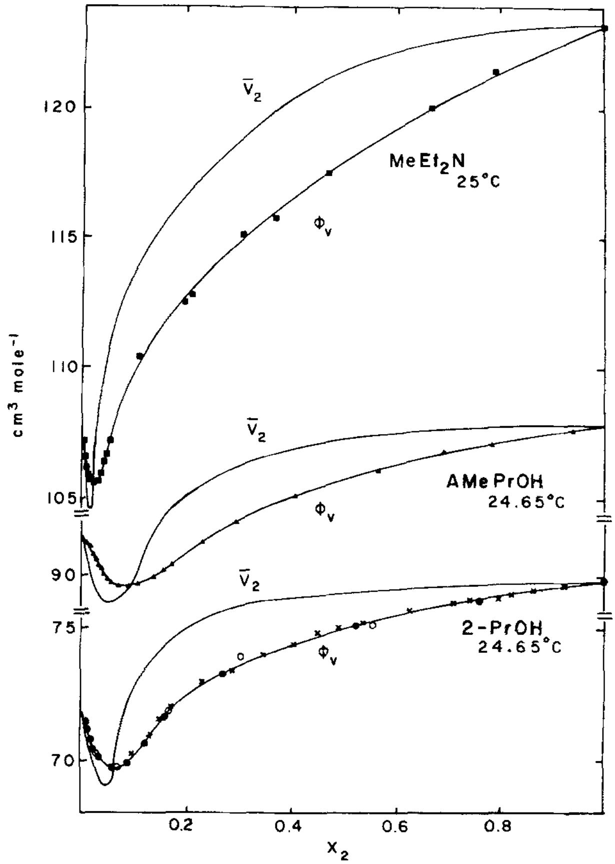


Fig. 1. Apparent and partial molal volumes of 2-propanol, diethylmethylamine and 2-amino-2-methyl-propanol in water. For 2-propanol; x Roux *et al*,(15) o Brunn and Hvidt;(13) ● present results.

in line with the others. They do not go through a minimum simply because of their solubility limit. The slope A_V of *neo*-PeOH is slightly more negative than that of *t*-PeOH suggesting stronger hydrophobic interactions. This could be expected from the geometry of the molecule. The bulky hydrophobic group being further away, there is less interference of the OH group on hydrophobic hydration.

4.2. Heat Capacities

The concentration dependence of some of the systems that were studied over the whole mole fraction range is shown in Fig. 3. While

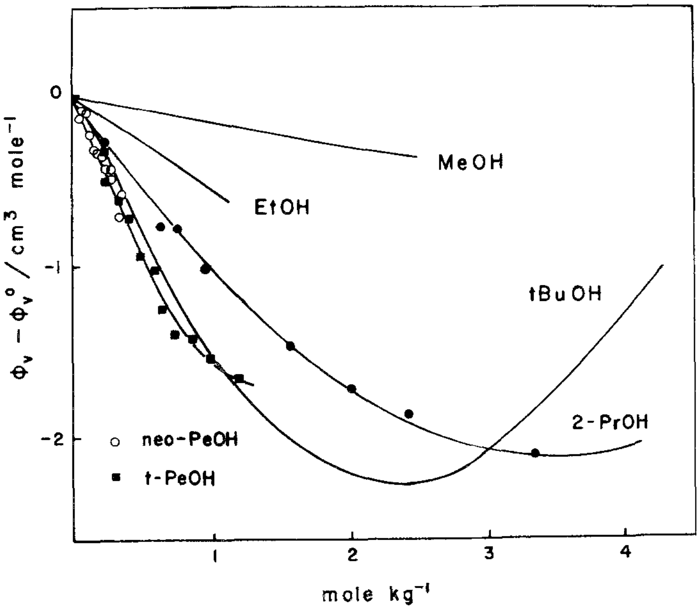


Fig. 2. Apparent molal volumes of branched alcohols in water at 25°C. Methanol and ethanol data from Jolicoeur and Lacroix[14] and *tert*-butanol data from de Visser *et al*[6]

ϕ_C of most hydrophobic solutes decreases in a rather regular way from infinite dilution to the pure liquid,[2,3] these systems behave like other alcohols[5,6] and some amines;[4] ϕ_C goes through a maximum or hump before decreasing rapidly to the molar heat capacity $C_{p,2}^o$. This effect increases with the hydrophobic character of the solute. The hydrophobic hydration, as measured by the magnitude of ϕ_C^o-$C_{p,2}^o$ increases in the order

AMePrOH < 2-PrOH < $MeEt_2N$ < Et_3N

and so does the magnitude of the humps. Presumably, if another CH_2 were added to AMePrOH, a hump would also be observed. The effect is also larger at low temperature with all systems.

The variation of the initial slopes is better seen in Fig. 4 where ϕ_C of the branched alcohols are plotted against m at 25°C. These data appear straightforward. As the size of the hydrophobic group increases, the initial slope A_C increases.[14] However, in actual fact, the situation is not that simple since quite different trends are observed with other systems and A_C varies significantly with temperature. With most

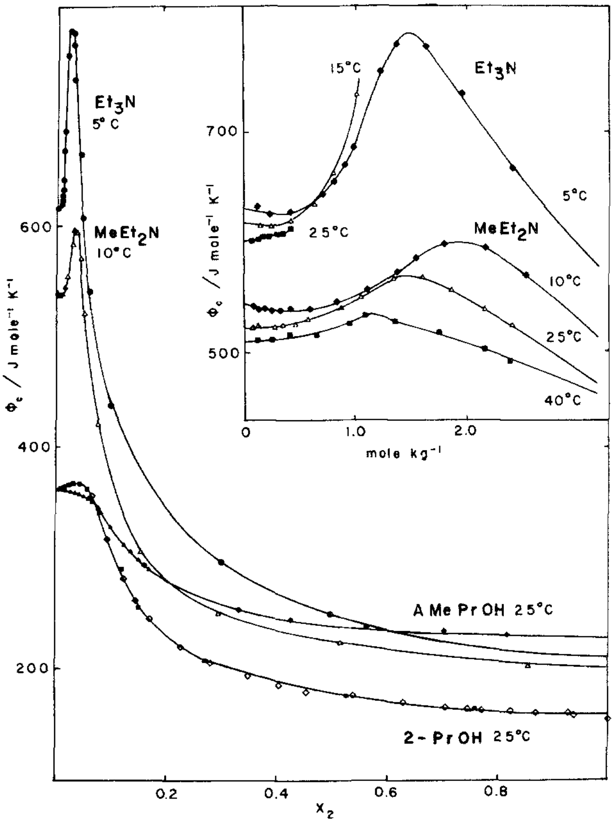


Fig. 3. Apparent molal heat capacities of some amines, alcohol and aminoalcohol in water. For 2-propanol, ◇ Roux *et al*;(15) ■ present results.

systems, A_C becomes increasingly more negative as the size or hydrophobic character increases.(2,3) With many amines, alcohols(1) and alkoxyalcohols(5) values for A_C are negative at low temperature but become positive at high temperature. There are therefore two effects which contribute to the concentration dependence of ϕ_C. The normal hydrophobic interaction between the two solutes leads to a reduction of the overall hydration effect (negative A_C). Superimposed on this there is a highly cooperative contribution with some systems which leads to the maximum or hump. This effect is related to the shift in equilibrium when the temperature is raised by 1°K. By analogy with kinetics it can be called the relaxation contribution. Jolicoeur *et al.*(26) and DeLisi *et al.*(27) have shown that association or micellization processes can lead to such a relaxation contribution. These relaxation effects with alcohols and alkoxyethanols were also observed with ultrasonic absorption,(28-30) light scattering,(8,31) NMR chemical shifts(9,32,33) and relaxations(34) and infrared spectra.(35)

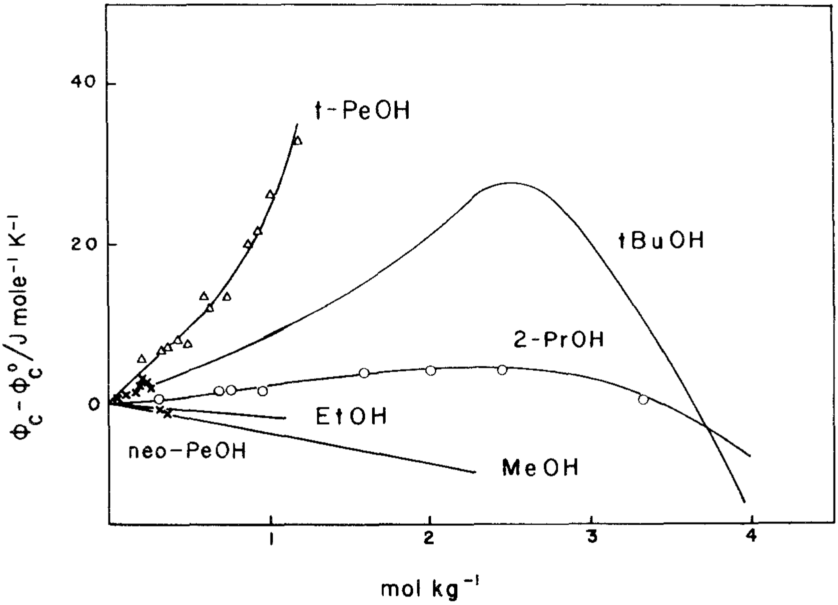


Fig. 4. Apparent molal heat capacities of branched alcohols at 25°C. Methanol and ethanol data from Jolicoeur and Lacroix,(14) *tert*-butanol data from de Visser *et al.*(6)

As in the case of volumes, the two pentanols fall roughly where we would expect them. With *neo*-PeOH a maximum is observed but the solubility limit prevents us from seeing the rapid decrease in ϕ_C beyond the maximum.

4.3. Expansibilities

The expansibilities ϕ_E are readily obtained from $d\phi_V/dT$ and are shown for some systems in Fig. 5. The infinite dilution ϕ_E^0 are much smaller than the molar values E_2^0 in agreement with hydrophobic hydration.(1) As in the case of ϕ_C, ϕ_E is a second derivative of the chemical potential. With such systems a positive relaxation contribution to ϕ_E is expected.(27) Therefore the maximum in ϕ_E, increasing with hydrophobic character, is not unexpected. It is not obvious however why the maximum in ϕ_E for $MeEt_2N$ should be sharper at 32.5°C than at 17.5°C. It could be that the maximum at 17.5°C is largely masked by the larger difference $\phi_E^o - E_2^o$.

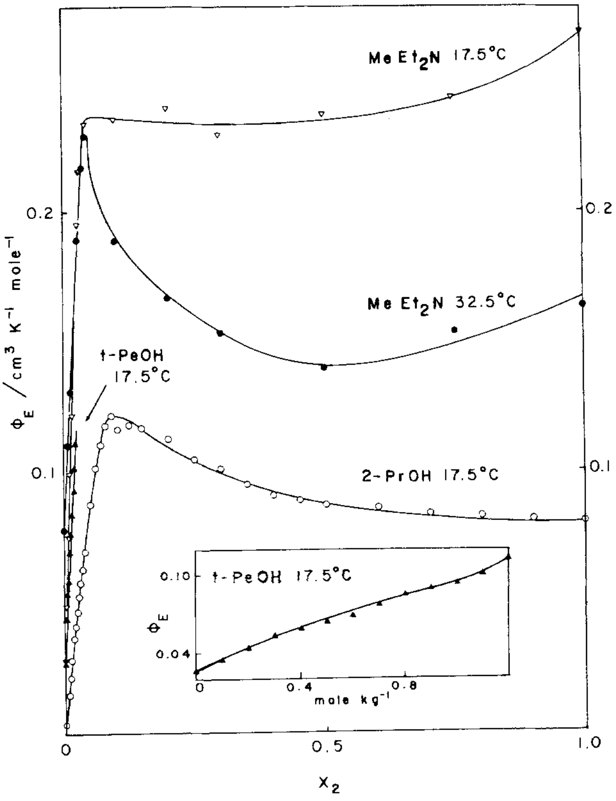


Fig. 5. Apparent molal expansibilities of diethylmethylamine, 2-propanol and *tert*-amylalcohol in water.

4.4. Microheterogeneity

The changes that take place in these aqueous-organic mixtures are better seen from the concentration dependence of $\bar{C}_{p,2}$. These $\bar{C}_{p,2}$, shown for Et_3N and $MeEt_2N$ in Fig. 6, change very rapidly for mole fractions between 0.03 to 0.06 and then tend to the value of the pure liquid solutes, $C_{p,2}^o$. The shape of these curves is similar to those of alcohols,(6) alkoxyethanols,(5) sodium decanoate and octylamine hydrobromide.(27) The two latter systems are well-known ionic surfactants and the sudden change in $\bar{C}_{p,2}$ is usually associated with the micellization process.

It was shown recently(27) that a phase-separation model predicts that the magnitude of the hump in ϕ_C and ϕ_E (relaxation term) should be given by

$$\Delta\phi_C = (\Delta H)^2/(RT)^2 \tag{2}$$

and

$$\Delta\phi_E = \Delta H \Delta V/(RT)^2 \tag{3}$$

where ΔV and ΔH are the volume and enthalpy of the phase change. This ΔH can be estimated from the partial molal relative enthalpies $\bar{L}_2$. While the enthalpies of mixing of many aqueous organic mixtures have been measured, few data points are normally available in the water-rich region. It is therefore difficult to estimate ΔH from enthalpies of mixing. Some enthalpies of dilution of *t*-BuOH in water exist(36) and from these a positive ΔH can be derived, leading to a relaxation contribution to ϕ_C. No such ΔH are apparent with aminoalcohols.(37) Systematic studies are presently under way to verify the relation between the relaxation contribution to ϕ_C and the enthalpies. Similarly, the positive values of both ΔV and ΔH would lead to a positive hump for ϕ_E as observed. The thermodynamic data therefore suggest that something similar to a microphase separation is occuring with some alcohols and amines in water, although these microphases can probably not be called micelles.

Many alcohols, alkoxyethanols and amines have a tendency to undergo phase separation with a lower critical solution temperature (LCST). For example, Et_3N has a LCST at 18.38°C corresponding to an amine concentration of 0.0543 mole fraction(38,39) and $MeEt_2N$ has a LCST at 49.42°C for an amine mole fraction of 0.098.(40) The thermodynamic properties (G, H, S) have been examined by a number of authors who have related the LCST to the molecular interactions in solution.(38-45) We therefore had expected at the beginning of this study that the microheterogeneity that was observed with the amines could be related to a microphase separation preceeding the macroscopic phase change. However, the changes are all sharper at lower temperature. Also, measurements of Et_3N at 25°C show no anomaly close to the two phase region. Therefore, there seems to be no direct relationship between the observed microheterogeneity and the existence of a LCST. Similar conclusions were reached with alkoxyethanols(5) and polyethers.(3)

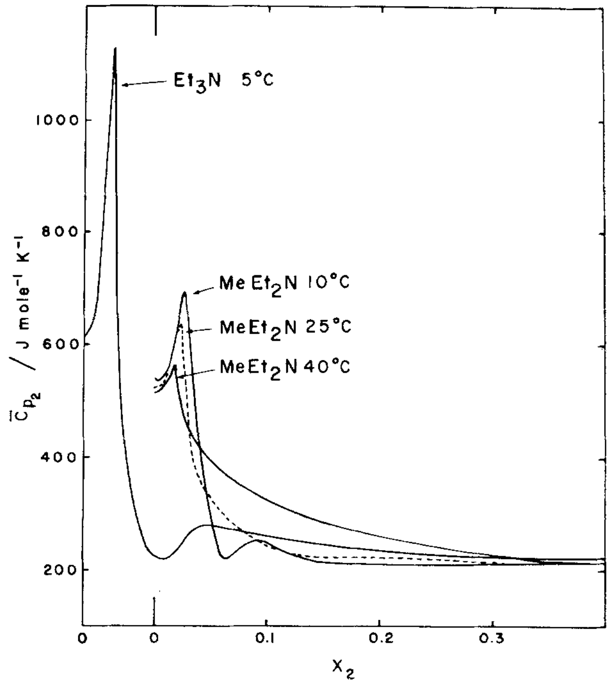
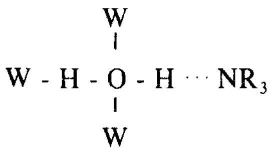


Fig. 6. Partial molal heat capacities of triethylamine and diethylmethylamine in water.

The question still remains as to why microheterogeneity in aqueous-organic systems is observed mostly with systems that can hydrogen bond with water. The work of Kingston and Symons(46) offers a plausible explanation. Most of the studies on alcohol-water mixtures strongly suggest the existence of time-average clathrate hydrates in the water-rich region, this structure collapsing when the ratio of alcohol to water exceeds that of clathrates.(8,9,31-35) Clathrate hydrates of trialkylamines also exist.(47) Kingston and Symons interpret the low-field chemical shifts of the hydroxy proton in the water-rich region of aqueous solutions of alcohols and Et$_3$N as the sum of two effects: (1) the increase in the structure of water due to the existence of time-average clathrates, (2) the acid-base type of interactions between the solute and water. The basic nature of alcohols and amines will lead to hydrogen-bonded structures such as



$$\begin{array}{c} \mathrm{W} \\ | \\ \mathrm{W-H-O-H\cdots NR_3} \\ | \\ \mathrm{W} \end{array}$$

which may reinforce the hydrophobic solvation. This acid-base effect is stronger with amines than with alcohols and could account for the larger humps in ϕ_C observed for amines in comparison with alcohols or alkoxyalcohols. The persistence of these humps to much higher temperatures in the case of amines is also consistent with this explanation. Hydrophobic solvation near the alkyl chains decreases rapidly with temperature while the acid-base interactions are much less temperature dependent.[46]

5. CONCLUSION

The concentration dependence of the thermodynamic properties of aqueous alcohol or amine solutions can be interpreted as follows; a) when a basic hydrophobic molecule like an alcohol or amine is added to water at infinite dilution the acid-base interactions with water will reinforce the normal hydrophobic hydration of the alkyl chain (large positive values of $\bar{C}_{p,2}^{\circ}$ - $C_{p,2}^{\circ}$ and negative values of $\bar{V}_2^{\circ}$ - V_2°, $\bar{E}_2^{\circ}$ - E_2° and $\bar{H}_2^{\circ}$ - H_2°). b) As the concentration is increased, hydrophobic interactions between solute molecules will tend to decrease the hydrophobic hydration (positive B_H and B_E and negative B_V and B_C). Superimposed on this effect there is a relaxation contribution to second derivative functions. The more structured entities have a stronger tendency to collapse with an increase in temperature (positive contribution to both ϕ_C and ϕ_E). c) As the structure around the solute collapses the solutes will rearrange themselves in a way such as to minimize contacts of the hydrophobic chains with water. The partial molal quantities of the solute are then similar to those of micellar solutes since the polar group still interacts strongly with the water while the hydrophobic part sees only other non-polar chains (strong decrease in $\bar{C}_{p,2}$ and increase in $\bar{V}_2$, $\bar{H}_2$ and $\bar{E}_2$. d) As further solutes are added, they dissolve preferentially with their hydrophobic chains in the microphases and the partial molal quantities remain essentially constant.

The qualitative picture of interactions in aqueous-organic mixtures should apply to all hydrophobic solutes to different degrees but the effects are largely amplified with basic or acidic hydrophobic solutes that can hydrogen bond with water. Also, as described recently by Lumry,(48) such characteristic changes in thermodynamic functions will be observed with all aqueous systems involving strong fluctuations such as micellization and protein association. Unfortunately, there does not seem to be any simple way of treating quantitatively the thermodynamics of these fluctuating systems at the present time.

ACKNOWLEDGMENT

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REFERENCES

1. C. de Visser, G. Perron, J. E. Desnoyers, W. J. H. Heuvelsland and G. Somsen, *J. Chem. Eng. Data* **22**, 74 (1977).
2. O. Kiyohara, G. Perron and J. E. Desnoyers, *Can. J. Chem.* **53**, 3263 (1975).
3. G. Roux, G. Perron and J. E. Desnoyers, *ibid* **56**, 2808 (1978).
4. O. Kiyohara, G. Perron and J. E. Desnoyers, *ibid* **53**, 2591 (1975).
5. G. Roux, G. Perron and J. E. Desnoyers, *J. Solution Chem.* **7**, 639 (1978).
6. C. de Visser, G. Perron and J. E. Desnoyers, *Can. J. Chem.* **55**, 856 (1977).
7. J. E. Desnoyers, R. DeLisi, C. Ostiguy and G. Perron in *Solution Chemistry of Surfactants*, Vol. 1, K. L. Mittal, ed., (Plenum Press, New York, 1979) p. 221.
8. K. Iwasaki and T. Fujiyama, *J. Phys. Chem.* **81**, 1908 (1977).
9. N. Muller, *J. Magn. Reson.* **28**, 203 (1977); see also *J. Phys. Chem.* **83**, 2041 (1979).
10. L. M. Prince, *Microemulsions, Theory and Practice*, (Academic Press, New York, 1977)
11. J. E. Desnoyers, R. Beaudoin, G. Perron and G. Roux, in *Chemistry for Energy*, Vol. 90, M. Tomlinson, ed., (ACS Symp. Ser., 1979), pg. 33.
12. M. A. Simard and J. L. Fortier, unpublished data.
13. S. G. Bruun and A. Hvidt, *Ber. Bunsengen Phys. Chem.* **84**, 930 (1977).
14. C. Jolicoeur and G. Lacroix, *Can. J. Chem.* **54**, 624 (1976).
15. A. Roux, J. P. Grolier and E. Wilheim, unpublished data.
16. R. C. Wilhoit and B. J. Zwolinski, *J. Phys. Chem. Ref. Data* **2**, 1 (1973).
17. S. Cabani, G. Conti and L. Lepori, *J. Phys. Chem.* **78**, 1030 (1974).
18. F. Shahidi, P. G. Farrell and J. T. Edward, *J. Chem Soc. Faraday Trans. I* **73**, 715 (1977).
19. B. E. Conway, R. E. Verrall and J. E. Desnoyers, *Trans. Faraday Soc.* **62**, 2738 (1966).
20. R. Arnaud, L. Avēdikian and J. P. Morel, *J. Chim. Phys.*, 45 (1972).
21. E. M. Arnett, W. B. Kover and J. V. Carter, *J. Am. Chem. Soc.* **91**, 4028 (1969).
22. S. Cabani, G. Conti, A. Martinelli and E. Matteoli, *J. Chem. Soc. Faraday Trans. I*

12, 2112 (1973).
23. N. Nichols, T. Sköld, C. Spink, J. Suurkuusk and I. Wadsö, *J. Chem. Thermodyn.* **8**, 1081 (1876).
24. (a) A. Bergström and G. Olofsson, *J. Solution Chem.* **4**, 535 (1975).
(b) J. A. Riddick and W. B. Bunger, "Organic Solvents", in *Techniques of Chemistry*, Vol. 2, A. Weissberger, ed., (Wiley-Interscience, New York, 1970), Chap. 1.
25. F. Franks and D. J. Reid in *Water: A Comprehensive Treatise*, Vol. 2, F. Franks, ed., (Plenum Press, New York, 1973), Chap. 5.
26. C. Jolicoeur, L. L. Lemelin and R. Lapalme, *J. Phys. Chem.* **83**, 2806 (1979).
27. R. DeLisi, G. Perron and J. E. Desnoyers, *Can. J. Chem* **58**, 959 (1980).
28. M. J. Blandamer, D. E. Clark, N. J. Hidden and M. C. R. Symons, *Trans. Faraday Soc.* **64**, 2691 (1968); see also M. J. Blandamer, N. J. Hidden, M. C. R. Symons and N. C. Treloar, *ibid* **64**, 3242 (1968).
29. R. J. Fanning and P. Kruus, *Can. J. Chem.* **48**, 2052 (1970).
30. K. Tamura, M. Mackawa and T. Yasunaga, *J. Phys. Chem.* **81**, 2122 (1977).
31. K. Iwasaki and T. Fujiyama, *J. Phys. Chem.* **83**, 463 (1979).
32. R. G. Anderson and M. C. R. Symons, *Trans. Faraday Soc.* **65**, 2550 (1969).
33. W. Y. Wen and H. G. Hertz, *J. Solution Chem.* **1**, 17 (1972).
34. J. Saunders and J. Van Dinter, in preparation.
35. M. J. Blandamer and M. C. R. Symons, *Hydrogen Bonded Solvent Systems*, A. K. Covington and P. Jones, eds., (Taylor and Francis, London, 1968).
36. J. E. Desnoyers, G. Perron, L. Avēdikian and J. P. Morel, *J. Solution Chem.* **5**, 631 (1976).
37. R. Okino, H. Touhara, K. Nakanishi and N. Watanabe, presented at the ACS-CSI Chemical congress, Honolulu, April 1979.
38. B. Chu and W. P. Kao, *Can. J. Chem.* **43**, 1803 (1965).
39. B. J. Hales, G. L. Bertrand and L. G. Hepler, *J. Phys. Chem.* **70**, 3970 (1966).
40. J. L. Copp, *Trans. Faraday Soc.* **51**, 1056 (1955).
41. J. L. Copp and D. H. Everett, *Faraday Soc. Discussions* **15**, 174 (1953).
42. J. L. Copp and D. H. Everett, *Trans. Faraday Soc.* **53**, 9 (1957).
43. G. L. Bertrand, J. W. Larson and L. G. Hepler, *J. Phys. Chem.* **72**, 4194 (1968).
44. E. M. Kartzmark, *Can. J. Chem.* **45**, 1089 (1967).
45. A. N. Campbell and E. M. Kartzmark, *Can. J. Chem.* **47**, 619 (1969).
46. B. Kingston and M. C. R. Symons, *J. Chem. Soc. Faraday Trans. 2.* **69**, 978 (1973).
47. M. Falk, *Can. J. Chem.* **69**, 1137 (1971).
48. R. Lumry, *Bioenergetics and Thermodynamics: Model Systems*, NATO Conference, Parma, Italy, May, 1979.