on the surface tension was investigated. The surface tension for water was obtained from the correlation by Jasper (*4*) as $\sigma/(\mathrm{mN\ m^{-1}}) = 75.83 - 0.1477(t/°\mathrm{C})$. Figure 2 shows the surface tensions for propylene glycol + water against mole fraction interpolated for temperatures of 30, 50, and 100 °C.

Connors and Wright (*5*) propose the equation

$$\sigma = \sigma_A - \left\{1 + \frac{bx_A}{1 - ax_A}\right\} x_B(\sigma_A - \sigma_B) \qquad (3)$$

where σ_A is the surface tension of water and σ_B the surface tension of the organic component to describe the effect of composition on the mixture surface tension. Hoke and Chen (*1*) showed that the surface tension parameters a and b are temperature dependent.

On the basis of the results given in Table II, the values for the surface tension parameters a and b are found from a nonlinear least-squares fit. Parameters are best described by

$$a = 0.9509 + 4.711 \times 10^{-6}(t/°\mathrm{C}) + 3.929 \times 10^{-7}(t/°\mathrm{C})^2$$

$$b = 0.7920 + 2.926 \times 10^{-6}(t/°\mathrm{C}) + 1.001 \times 10^{-7}(t/°\mathrm{C})^2$$

for temperatures between 10 °C and the normal boiling point of the propylene glycol + water mixture. The average deviation for a and b is less than 0.01%. Propylene glycol + water surface tensions at any temperature between 10 °C and the normal boiling point can be calculated using the pure component surface tension correlations and eq 3.

Acknowledgment

We thank Professor John C. Chen for providing the experimental equipment.

Nomenclature

a = surface tension parameter defined in eq 3
b = surface tension parameter defined in eq 3
t = temperature
T_c = critical temperature
T_c' = pseudocritical temperature defined in eq 2
T_r' = reduced temperature, T/T_c'
x = mole fraction

Greek Letters

α = surface tension parameter defined in eq 1
β = surface tension parameter defined in eq 1
σ = surface tension

Subscripts

A = water
B = propylene glycol

Registry No. Propylene glycol, 57-55-6.

Literature Cited

(1) Hoke, B. C., Jr.; Chen, J. C. *J. Chem. Eng. Data* **1991**, *36*, 322.
(2) Sugden, S. *J. Chem. Soc., Trans.* **1922**, *121*, 858.
(3) Jones, W. S.; Tamplin, W. S. In *Glycols*; Curme, G. O., Jr., Johnston, F., Eds.; Reinhold Publishing Corp.: New York, 1952; p 210.
(4) Jasper, J. J. *J. Phys. Chem. Ref. Data* **1972**, *1*, 841.
(5) Connors, K. A.; Wright, J. L. *Anal. Chem.* **1989**, *61*, 194.

Received for review November 25, 1991. Accepted March 26, 1992.

Partial Molar Volumes of Transfer at Infinite Dilution of Some Electrolytes in Dimethyl Sulfoxide–Water Mixtures at 298.15 K

Eugenio García-Pañeda, Pilar Pérez-Tejeda, Cayetano Yanes, and Alfredo Maestre*

Departamento de Química Física, Facultad de Química, Universidad de Sevilla, 41012 Sevilla, Spain

Limiting partial molar volumes, V_2^∞, of LiCl, NaCl, KCl, NaBr, KBr, KI, $NaPh_4B$, and Ph_4AsCl have been determined in dimethyl sulfoxide (DMSO)–water mixtures at 298.15 K with a vibrating tube digital densimeter. V_2^∞ values for alkali-metal halides with a common cation or anion increase with the increasing size of the counterion and decrease with the increase of the DMSO composition. This last effect is also shown in the case of $NaPh_4B$ and Ph_4AsCl. Partial molar volumes of transfer from water to DMSO–water mixtures, $\Delta_t V_2^\infty$, have been calculated in order to obtain a measure of the difference in electrolyte–solvent interactions between water and the different mixtures. Observed effects show a decrease in $\Delta_t V_2^\infty$ with the DMSO composition for all electrolytes studied, but whereas $\Delta_t V_2^\infty$ values for Ph_4AsCl are negative, those for $NaPh_4B$ are positive at all DMSO compositions.

Introduction

The partial molar volume at infinite dilution, V_2^∞, is an appropriate thermodynamic quantity for elucidating the nature of solute–solvent interactions. While extensive data have been obtained for V_2^∞ of electrolytes in water (*1*) and nonaqueous solvent (*2–9*), less attention has been paid to mixed aqueous solvents (*10–13*). Possibly, due to the large quantity of experimental work necessary, proof that some of the work on mixed aqueous solvents has been done at only one electrolyte concentration (*12*, *13*). This paper reports limiting partial volumes of some electrolytes in dimethyl sulfoxide (DMSO)–water mixtures at 298.15 K. DMSO was chosen because of its extensive application in chemistry, pharmacy, and industry.

Experimental Section

Dimethyl sulfoxide (Merck, G.R., stated purity >99.5 mol %, H_2O <0.03%) was kept over thermally activated 4-Å molecular sieves prior to use. Nonane (Fluka, 74252, >99 mol %) was used as received. The salts LiCl, NaCl, KCl, NaBr, and KI were reagents (Merck) and were used after drying overnight at 393.15 K. $NaPh_4B$ (Merck, G.R.) was dried at 353.15 K in a vacuum desiccator for 48 h. $Ph_4AsCl{\cdot}H_2O$ (Merck, G.R.) was prepared as an anhydrous salt according to the literature recommended method (*15*). Water was obtained from a Milli-RO and Milli-Q water system (Millipore, $\sigma \approx 10^{-6}$ S m^{-1}). Both DMSO and water were degassed prior to making solutions by weight.

The solution densities were measured at 298.15 K with an Anton Paar (DMA 60/602) vibrating tube densimeter with precision of ±3 × 10^{-3} kg m^{-3}. The temperature in the measuring cell was regulated through a cascade water bath apparatus (Heto). This system permits stability within ±0.01 K for a period of several days as checked by a digital precision thermometer

0021-9568/92/1737-0333$03.00/0

Table I. Molalities m_2, Densities ρ, and Apparent Molar Volumes $\phi_{v,2}$ for Several Electrolytes in x DMSO + $(1 - x)$ Water at 298.15 K

m_2/(mol kg^{-1})	$10^{-3}\rho$/(kg m^{-3})	$10^6\phi_{v,2}$/(m^3 mol^{-1})	m_2/(mol kg^{-1})	$10^{-3}\rho$/(kg m^{-3})	$10^6\phi_{v,2}$/(m^3 mol^{-1})	m_2/(mol kg^{-1})	$10^{-3}\rho$/(kg m^{-3})	$10^6\phi_{v,2}$/(m^3 mol^{-1})
				LiCl (x = 0.2570)				
0.0000	1.082 76		0.1529	1.087 11	14.82	0.2574	1.089 97	15.16
0.0499	1.084 20	14.52	0.1758	1.087 74	14.92	0.2999	1.091 17	15.11
0.0753	1.084 93	14.52	0.1970	1.088 37	14.78			
0.0998	1.085 62	14.67	0.2223	1.089 11	14.70			
				NaCl (x = 0.2570)				
0.0502	1.084 75	20.12	0.1257	1.087 70	20.36	0.1925	1.090 36	20.16
0.0757	1.085 76	20.12	0.1491	1.088 65	20.17	0.2248	1.091 61	20.23
0.0984	1.086 65	20.18	0.1685	1.089 40	20.24	0.2539	1.092 72	20.33
				KCl (x = 0.2570)				
0.0518	1.085 10	30.26	0.1529	1.089 67	30.12	0.2240	1.092 84	30.20
0.1015	1.087 35	30.16	0.1794	1.090 87	30.08	0.2473	1.093 89	30.16
0.1254	1.088 44	30.07	0.1971	1.091 65	30.14			
				NaBr (x = 0.2570)				
0.0486	1.086 57	28.07	0.1224	1.092 36	27.89	0.2015	1.098 50	28.00
0.0742	1.088 58	27.98	0.1437	1.094 01	27.97	0.2216	1.100 07	27.96
0.1000	1.090 60	27.96	0.1743	1.096 42	27.84			
				KBr (x = 0.2570)				
0.0744	1.089 09	37.11	0.1749	1.097 46	37.71	0.2484	1.103 61	37.59
0.1216	1.093 07	37.24	0.1974	1.099 38	37.52	0.2968	1.107 63	37.58
0.1494	1.095 35	37.60	0.2231	1.101 50	37.61			
				KI (x = 0.2570)				
0.0501	1.088 72	51.51	0.1244	1.097 38	52.37	0.1997	1.105 99	52.96
0.0755	1.091 70	51.83	0.1463	1.099 89	52.62	0.2237	1.108 69	53.18
0.0994	1.094 48	52.19	0.1619	1.101 69	52.67	0.2493	1.111 56	53.36
				$NaPh_4B$ (x = 0.2570)				
0.0521	1.084 11	293.60	0.1472	1.086 49	293.45	0.1954	1.088 25	293.20
0.0762	1.084 74	293.37	0.1598	1.086 95	293.48	0.2190	1.086 80	293.41
0.1216	1.085 87	293.41	0.1666	1.087 69	293.22	0.2735	1.089 57	292.99
				Ph_4AsCl (x = 0.2570)				
0.0490	1.086 84	314.55	0.1216	1.092 76	313.76	0.1912	1.098 15	313.68
0.0668	1.088 34	314.06	0.1537	1.095 27	313.75			
0.1017	1.091 17	313.83	0.1558	1.095 40	313.93			
				LiCl (x = 0.3498)				
0.0000	1.092 99		0.1283	1.096 91	13.16	0.2209	1.099 64	13.51
0.0508	1.094 55	13.04	0.1326	1.097 05	13.11	0.2515	1.100 55	13.53
0.0781	1.095 40	12.94	0.1765	1.098 34	13.34			
0.0959	1.095 92	13.18	0.1975	1.098 94	13.49			
				NaCl (x = 0.3498)				
0.0394	1.094 63	18.58	0.0519	1.095 13	18.88	0.0934	1.096 78	19.42
0.0436	1.094 81	18.46	0.0663	1.095 71	19.09	0.0937	1.096 79	19.46
0.0517	1.095 12	18.95	0.0792	1.096 23	19.15			
				KCl (x = 0.3498)				
0.0471	1.095 21	28.71	0.1157	1.098 31	29.60	0.2097	1.102 47	30.11
0.0743	1.096 45	29.12	0.1441	1.099 60	29.65	0.2129	1.102 68	29.85
0.0945	1.097 37	29.30	0.1792	1.101 21	29.59	0.2614	1.104 80	30.06
				NaBr (x = 0.3498)				
0.0448	1.096 55	27.46	0.1413	1.104 14	27.82	0.2041	1.109 12	27.58
0.0982	1.100 76	27.70	0.1478	1.104 69	27.56	0.2284	1.110 98	27.74
0.1130	1.101 89	27.97	0.1771	1.106 90	28.05			
				KBr (x = 0.3498)				
0.0489	1.097 18	36.97	0.1160	1.102 88	37.20	0.1898	1.109 12	37.20
0.0704	1.099 02	36.97	0.1514	1.105 87	37.21	0.2212	1.111 75	37.26
0.0829	1.100 07	37.16	0.1727	1.107 68	37.19	0.2445	1.113 70	37.28
				KI (x = 0.3498)				
0.0401	1.097 83	50.50	0.1398	1.109 68	51.15	0.2458	1.122 25	50.87
0.0672	1.101 07	50.83	0.1566	1.111 77	50.65			
0.1243	1.107 90	50.81	0.1914	1.115 78	51.15			
				$NaPh_4B$ (x = 0.3498)				
0.0498	1.094 08	294.51	0.1130	1.095 41	294.53	0.1797	1.096 81	294.29
0.0700	1.094 53	294.28	0.1361	1.095 90	294.43	0.2369	1.098 01	294.02
0.0963	1.095 06	294.55	0.1656	1.096 48	294.53	0.2614	1.098 55	293.82

Table I (Continued)

m_2/ (mol kg^{-1})	$10^{-3}\rho$/ (kg m^{-3})	$10^6\phi_{v,2}$/ (m^3 mol^{-1})	m_2/ (mol kg^{-1})	$10^{-3}\rho$/ (kg m^{-3})	$10^6\phi_{v,2}$/ (m^3 mol^{-1})	m_2/ (mol kg^{-1})	$10^{-3}\rho$/ (kg m^{-3})	$10^6\phi_{v,2}$/ (m^3 mol^{-1})
Ph_4AsCl (x = 0.3498)								
0.0455	1.096 80	311.90	0.0807	1.099 69	311.79	0.1195	1.102 82	311.48
0.0564	1.097 70	311.86	0.0944	1.100 82	311.47	0.1541	1.105 55	311.36
0.0703	1.098 86	311.63	0.1030	1.101 51	311.46	0.1809	1.107 54	311.68
LiCl (x = 0.5665)								
0.0000	1.099 21		0.1273	1.103 66	9.59	0.2028	1.106 20	9.97
0.0501	1.100 96	9.63	0.1594	1.104 72	9.91			
0.1087	1.103 04	9.37	0.1867	1.105 62	10.09			
NaCl (x = 0.5665)								
0.0799	1.102 61	17.88	0.1292	1.104 67	18.10	0.1800	1.106 75	18.37
0.1039	1.103 62	17.96	0.1568	1.105 80	18.27	0.2087	1.107 86	18.72
KCl (x = 0.5665)								
0.0521	1.101 81	26.31	0.0751	1.102 94	26.64	0.0998	1.104 14	26.81
0.0666	1.102 56	26.11	0.0904	1.103 70	26.60	0.1128	1.104 74	27.12
NaBr (x = 0.5665)								
0.0506	1.103 44	24.29	0.1015	1.107 60	25.01	0.1521	1.111 78	24.93
0.0761	1.105 54	24.60	0.1265	1.109 69	24.81	0.2037	1.115 99	25.05
KBr (x = 0.5665)								
0.0487	1.103 55	34.41	0.0877	1.107 05	34.00	0.1585	1.113 29	34.49
0.0773	1.106 09	34.42	0.1252	1.110 31	34.54	0.1764	1.114 83	34.49
KI (x = 0.5665)								
0.0517	1.105 59	48.61	0.1481	1.117 40	48.57	0.2012	1.124 02	47.89
0.0748	1.108 45	48.40	0.1758	1.120 89	48.01	0.2218	1.126 54	47.86
$NaPh_4B$ (x = 0.5665)								
0.0495	1.100 22	294.20	0.1203	1.101 76	293.12	0.1954	1.103 33	292.79
0.0788	1.100 88	293.65	0.1498	1.102 38	292.98	0.2195	1.103 83	292.69
0.0977	1.101 28	293.26	0.1751	1.102 91	292.87			
Ph_4AsCl (x = 0.5665)								
0.0483	1.103 26	310.45	0.1302	1.109 85	310.37	0.1962	1.114 86	310.58
0.0740	1.105 37	310.41	0.1505	1.111 41	310.47			
0.1025	1.107 66	310.39	0.1755	1.113 30	310.58			
LiCl (x = 0.6748)								
0.0000	1.098 82		0.1238	1.103 29	8.65	0.2191	1.106 69	8.76
0.0514	1.100 71	8.13	0.1483	1.104 18	8.61	0.2930	1.109 42	9.04
0.0725	1.101 48	8.16	0.1699	1.104 99	8.44			
0.0958	1.102 32	8.28	0.2045	1.106 16	8.79			
NaCl (x = 0.6748)								
0.0132	1.099 41	16.12	0.0303	1.100 17	16.26	0.0381	1.100 51	16.40
0.0182	1.099 63	16.25	0.0342	1.100 35	16.15	0.0440	1.100 77	16.47
NaBr (x = 0.6748)								
0.0252	1.100 95	23.46	0.0358	1.101 84	23.62	0.0488	1.102 93	23.73
0.0279	1.101 18	23.56	0.0435	1.102 48	23.82	0.0596	1.103 83	23.94
0.0310	1.101 43	23.92	0.0487	1.102 92	23.84			
KBr (x = 0.6748)								
0.0477	1.103 19	32.08	0.1169	1.109 47	32.52	0.1777	1.114 91	32.82
0.0631	1.104 59	32.41	0.1369	1.111 27	32.61	0.2184	1.118 51	33.05
0.0856	1.106 65	32.31	0.1593	1.113 29	32.65	0.2471	1.121 08	33.02
KI (x = 0.6748)								
0.0242	1.101 86	46.82	0.0448	1.104 48	46.27	0.1229	1.114 25	46.42
0.0309	1.102 72	46.35	0.0681	1.107 43	46.02	0.1824	1.121 68	46.34
$NaPh_4B$ (x = 0.6748)								
0.0513	1.099 94	293.06	0.0930	1.100 90	292.37	0.1386	1.101 93	292.04
0.0634	1.100 26	292.25	0.1235	1.101 59	292.14	0.1644	1.102 51	291.88
0.0743	1.100 47	292.63	0.1376	1.101 92	291.97			
Ph_4AsCl (x = 0.6748)								
0.0459	1.102 83	307.66	0.0870	1.106 37	307.15	0.1228	1.109 34	307.22
0.0730	1.105 16	307.46	0.1104	1.108 32	307.20	0.1280	1.109 75	307.36
$NaPh_4B$ (x = 1.0)								
0.0000	1.095 59		0.0999	1.098 06	291.12	0.1720	1.099 82	290.76
0.0522	1.096 89	291.29	0.1227	1.098 64	290.85	0.1968	1.100 39	290.78
0.0737	1.097 43	291.09	0.1482	1.099 26	290.77			
Ph_4AsCl (x = 1.0)								
0.0523	1.100 42	303.92	0.1238	1.106 83	303.52	0.1913	1.112 50	303.93
0.0777	1.102 75	303.54	0.1480	1.108 85	303.95			
0.1011	1.104 83	303.57	0.1746	1.111 08	304.06			

Table II. Partial Molar Volumes V_2^∞ at Infinite Dilution in x DMSO + $(1 - x)$ Water Mixtures at 298.15 K

	$V_2^\infty/(\mathrm{cm^3\ mol^{-1}})$ at various x				
electrolyte	0.2570	0.3498	0.5665	0.6748	1.0
LiCl	14.1 ± 0.4	12.4 ± 0.3	8.9 ± 1.0	7.4 ± 0.4	4.7,[a] 10.4[b]
NaCl	20.0 ± 0.3	16.9 ± 0.6	16.5 ± 0.6	15.8 ± 0.6	15.0,[a] 12.3[b]
KCl	30.2 ± 0.2	27.9 ± 0.5	25.0 ± 1.3	24.3 ± 1.7[e]	23.8,[a] 20.0[c]
NaBr	28.1 ± 0.3	27.4 ± 0.8	23.7 ± 0.8	22.9 ± 0.8	19.4,[a] 19.9[b]
KBr	36.7 ± 0.6	36.8 ± 0.2	34.1 ± 1.0	31.4 ± 0.3	28.1,[a] 27.7[b]
KI	49.9 ± 0.3	50.4 ± 0.8	49.3 ± 1.0	46.6 ± 0.8	42.8,[a] 41.9[b]
$NaPh_4B$	294.0 ± 0.5	295.0 ± 0.7	295.2 ± 0.8	294.0 ± 0.9	291.8 ± 0.2,[d] 290[b]
Ph_4AsCl	315.0 ± 1.0	312.2 ± 0.7	310.2 ± 0.4	308.1 ± 0.5	303.3 ± 1.0,[d] 304[c]

[a] Reference 6. [b] Reference 9. [c] Reference 5. [d] This work. [e] From additivity law.

(Anton Paar DT 100-20). The whole system was placed in a thermostated room at ±0.5 K. The densimeter was calibrated everyday by use of water (ρ = 997.045 kg m^{-3}) (*16*) and nonane (ρ = 713.85 kg m^{-3}) (*17*).

In order to test the instrument, densities of aqueous NaCl solutions were determined and compared favorably to data from the literature (*18*). The partial molar volume at infinite dilution of NaCl was found to be 16.63 ± 0.15 × 10^{-6} m^3 mol^{-1}, which agreed with those tabulated by Millero (*1*). Nevertheless, density values for aqueous DMSO solutions had an uncertainty of ±10 × 10^{-3} kg m^{-3}. This loss of precision in relation to aqueous solutions is also observed by other researchers with acetonitrile aqueous solutions (*13*). The reason for this discrepancy is not clear at present. Densities of DMSO–water binary mixtures (Table I) agree well with the corresponding literature values (*19*, *20*).

Results and Discussion

The apparent molar volumes, ϕ_V, of electrolytes in DMSO–water mixtures or pure DMSO were evaluated from experimentally measured densities with the equation

$$\phi_V = \frac{(\rho^\circ - \rho)}{m\rho\rho^\circ} + \frac{M_2}{\rho} \tag{1}$$

where ρ° is the density of water or DMSO–water solvent, ρ is the density of electrolyte solutions, and M and m are the molar mass and the molality of the electrolyte, respectively. The values of ϕ_V determined via eq 1 at various concentrations, along with the respective densities, are given in Table I. Since ϕ_V's varied linearly with $m^{1/2}$ over the concentration range studied, the limiting partial molar volume of the electrolyte, $V_2^\infty = \phi_V^\infty$, was obtained by least-squares fitting of the results to the Masson equation

$$\phi_V = \phi_V^\infty + S_V^* m^{1/2} \tag{2}$$

where S_V^* is the experimental slope. Values of V_2^∞ together with their 95% confidence limits are presented in Table II. As can be observed, the additivity law shows in all instances to be smaller than ±2 cm^3 mol^{-1}.

We can see from Table II that V_2^∞ values for alkali-metal halides with a common cation or anion increase on increasing the ionic size of the ion and decrease with the increase of DMSO composition.

Table III. Partial Molar Volumes of Transfer of Electrolytes (2) at Infinite Dilution $\Delta_t V_2^\infty$ from Water to x DMSO + $(1 - x)$ Water at 298.15 K

	$\Delta_t V_2^\infty/(\mathrm{cm^3\ mol^{-1}})$ at various x				
electrolyte	0.2570	0.3498	0.5665	0.6748	1.0
LiCl	−2.8	−4.5	−8.0	−9.5	−12.2
NaCl	3.4	0.3	−0.1	−0.8	−1.6
KCl	3.4	1.1	−1.8	−2.5	−3.0
NaBr	4.6	3.9	0.2	−0.6	−4.1
KBr	3.0	3.1	0.4	−2.3	−5.6
KI	4.8	5.3	4.2	1.5	−2.6
$NaPh_4B$	17.6	18.6	18.8	17.6	15.4
Ph_4AsCl	−3.5	−6.3	−8.3	−10.4	−15.2

A measure of the difference in solute–solvent interactions between water (w) and DMSO–water or pure DMSO (s) can be obtained by means of partial molar volumes of transfer at infinite dilution, $\Delta_t V_2^\infty$ (w → s). In this sense, we have calculated $\Delta_t V_2^\infty$ values from Table I and those of water (*1*); the results are presented in Table III. It can be seen that the increasing of DMSO produces a decrease in $\Delta_t V_2^\infty$ values. This effect is more pronounced for LiCl than for the other alkali-metal halides. Moreover, reverse trends for $NaPh_4B$ in relation to Ph_4AsCl are observed. In binary DMSO–water mixtures solvent–solvent interactions depend on the DMSO composition, and three different regions can be considered (*21*, *22*): (1) a highly water-rich region, a quasiclathrate structure, (2) a region where further addition of DMSO involves strong DMSO–water interactions, forming hydrogen-bonded associate DMSO–water, which are maximized at $x_{DMSO} \approx 0.33$, and (3) a region where dipole–dipole interactions between water and DMSO molecules appear. The presence of electrolytes in the binary mixture DMSO–H_2O must modify solvent–solvent interactions, in the sense of preventing or facilitating them, this effect being dependent on the kind of electrolyte. Transfer thermodynamic measurements of ions through the whole range of DMSO, such as $\Delta_t G_i^\infty$, $\Delta_t H_i^\infty$, and $\Delta_t S_i^\infty$, show no indication of preferential solvation (*23*). However, Petrella et al. (*24*) on the basis of ionic conductivity suggest that alkali metals are preferentially solvated by water in water-rich regions. On the other hand, pure DMSO solvates cations stronger than anions (*5*, *6*). It is difficult to explain the varions of $\Delta_t V_2^\infty$ in Table III from ionic effects since an electrolyte is treated as a whole. The evaluation of individual partial molar quantities of ions is made by using some extrathermodynamic assumptions (*25*). Nevertheless, in the concrete case of volume, single ionic contributions to V_2^∞ can be experimentally obtained using ultrasonic vibration potential (UVP) (*26*) or sedimentation potential (SP) (*27*) measurements. Extrathermodynamic methods (*28*) and UVP or SP measurements agree well when the solvent is water, but in dipolar aprotic solvents, such as DMSO, or their aqueous mixtures in the nonaqueous solvent-rich region, significant differences are observed (*6*, *28*). Lankford and Criss (*9*) have noted that in dipolar aprotic solvents the only way to obtain single ionic contributions to V_2^∞ is from UVP or SP measurements. Unfortunately, in DMSO–water mixtures these measurements are lacking and the ionic partial molar volumes, V_i^∞, obtained from some extrathermodynamic assumption would be doubious, especially in our case where the DMSO composition is fairly high.

Registry No. DMSO, 67-68-5; LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; NaBr, 7647-15-6; KBr, 7758-02-3; KI, 7681-11-0; $NaPh_4B$, 143-66-8; Ph_4AsCl, 507-28-8.

Literature Cited

(1) Millero, F. J. In *Water and Aqueous Solutions* (*structure*, *Thermodynamics*, *and Transport Processes*); Horne, R. A., Ed.; Wiley-Interscience: New York, 1972; Chapter 13.
(2) Gopal, R.; Agarwal, D. K.; Kumar, R. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1973.
(3) Kawaizumi, F.; Zana, R. *J. Phys. Chem.* **1974**, *78*, 627, 1099.

J. Chem. Eng. Data **1992**, *37*, 337–338

(4) Sen, U. *J. Phys. Chem.* **1977**, *81*, 35.
(5) Dack, M. R. J.; Bird, K. J.; Parker, A. J. *Aust. J. Chem.* **1975**, *28*, 955.
(6) Kale, K. M.; Zana, R. *J. Solution Chem.* **1977**, *6*, 733.
(7) Krumgalz, B. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1887.
(8) Zana, R.; Desnoyers, J. E.; Perron, G.; Kay, R. L.; Lee, K. *J. Phys. Chem.* **1982**, *86*, 3996.
(9) Lankford, J. I.; Criss, C. M. *J. Solution Chem.* **1987**, *16*, 753.
(10) McDonald, D. D.; Hyne, J. B. *Can. J. Chem.* **1970**, *48*, 2416.
(11) Hirakawa, H.; Nomura, H.; Kawaizumi, F. *J. Phys. Chem.* **1989**, *93*, 3784.
(12) Hefter, G. T.; Groller, J. P. E.; Roux, A. H. *J. Solution Chem.* **1989**, *18*, 229.
(13) Hefter, G. T.; Groller, J. P. E.; Roux, A. H.; Roux-Desgranges, G. *J. Solution Chem.* **1990**, *19*, 207.
(14) Kawaizumi, F.; Inone, Y.; Nomura, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 510.
(15) Krishnan, C. V.; Friedman, H. L. *J. Phys. Chem.* **1969**, *73*, 3934.
(16) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 91.
(17) Ortega, J.; Paz-Andrade, M. I. *J. Chem. Eng. Data* **1986**, *31*, 231.
(18) Vaslow, F. *J. Phys. Chem.* **1966**, 70, 2286.
(19) Cowie, J. M. G.; Toporowski, P. M. *Can. J. Chem.* **1961**, *39*, 2240.
(20) Pruett, D. J.; Felker, L. K. *J. Chem. Eng. Data* **1985**, *30*, 452.
(21) Werblan, L.; Lesinski, J. *Pol. J. Chem.* **1978**, *52*, 1211.
(22) Kinart, C. M.; Kinart, W. J.; Skulski, L. *Pol. J. Chem.* **1986**, *60*, 879.
(23) Cox, B. G.; Waghorne, W. E. *Chem. Soc. Rev.* **1980**, *9*, 380.
(24) Petrella, G.; Petrella, M.; Castagnolo, M.; Dell'Atti, A.; De Giglio, A. *J. Solution Chem.* **1981**, *10*, 129.
(25) Marcus, Y. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 2965.
(26) Zana, R.; Yeager, E. B. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum Press: New York, 1982; Vol. 14, pp 1–60.
(27) Hirakawa, H. *J. Phys. Chem.* **1987**, *33*, 3452.
(28) Marcus, Y. *Ion Solvation*; Wiley: New York, 1985; Chapter 6.

Received for review October 21, 1991. Revised March 9, 1992. Accepted March 23, 1992.

Vapor–Liquid Equilibria for Carbon Dioxide + 1-Pentanol

David W. Jennings, Franchot Chang, Vivian Bazaan, and Amyn S. Teja*

School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Vapor–liquid equilibria have been measured for CO_2 + 1-pentanol at 314.6, 325.9, and 337.4 K using a high-pressure flow apparatus. The pressure in the experiments ranged from 5.176 to 11.983 MPa. The results show that the phase behavior of CO_2 + 1-pentanol is similar to the phase behavior observed for CO_2 + ethanol and CO_2 + 1-butanol.

Introduction

This work forms part of a continuing study of CO_2 + alkanols (*1*) of interest in the extraction of biomolecules (*2–4*) with supercritical CO_2 + alkanols, extraction of alkanols from aqueous solutions with carbon dioxide (*5–8*), and the production of alkanols from syngas (*9*). Although much attention has been focused on CO_2 + methanol and CO_2 + ethanol systems, very little attention has been paid to CO_2 + higher alkanol systems. In fact, no previous vapor–liquid equilibrium measurements have been reported in the literature for CO_2 + 1-pentanol with the exception of the critical properties of dilute mixtures measured by Gurdial et al. (*10*).

Experimental Section

The experimental procedure and apparatus have been described in detail previously (*1*), and only brief details are given below. Carbon dioxide from a cylinder and 1-pentanol from a reservoir were mixed and pumped through a series of coils and static mixers placed inside a constant-temperature air bath. Vapor–liquid equilibrium was attained during the pumping process. After equilibration, the phases were separated in a high-pressure stainless steel view cell (similar to a Jerguson level gauge) and each phase was depressurized across a micrometering valve. The pentanol from each phase was condensed and collected in a cold trap, while the carobn dioxide was allowed to pass through a wet test meter. Equilibrium phase compositions were calculated from the weights of the pentanol collected and the volume of carbon dioxide measured by the wet test meters. Small corrections were made for the residual pentanol not condensed and for the carbon dioxide dissolved in the condensed pentanol. Typically, 4–6 liquid samples and 3–5 vapor samples were collected. The reported compositions represent an average of all the samples equilibrated at the desired pressure and temperature. Additionally, to verify that equilibrium conditions had been attained, some experiments at a given temperature and pressure were repeated at different flow rates. No changes in equilibrium compositions with flow rates were detected.

Table I. Experimental Vapor–Liquid Equilibrium Data for CO_2 + 1-Pentanol

P/MPa	T/K	x_{CO_2}	y_{CO_2}
5.178	314.7	0.3368	0.9991
6.157	314.8	0.4135	0.9989
6.902	314.7	0.4850	0.9984
7.598	314.7	0.5657	0.9977
8.074	314.3	0.6714	0.9969
	av: 314.6		
6.164	325.9	0.3367	0.9983
6.943	326.0	0.4044	0.9978
7.667	325.9	0.4612	0.9971
8.274	326.0	0.5077	0.9965
8.977	326.0	0.5695	0.9951
9.660	326.0	0.6433	0.9924
10.342	325.8	0.7516	0.9781
10.556	325.9	0.7944	0.9617
	av: 325.9		
5.585	337.4	0.2834	0.9975
6.943	337.3	0.3583	0.9969
7.639	337.4	0.3976	0.9963
8.294	337.5	0.4346	0.9958
8.956	337.4	0.4767	0.9949
9.660	337.4	0.5220	0.9936
10.418	337.4	0.5772	0.9911
11.052	337.4	0.6300	0.9876
11.983	337.5	0.7185	0.9745
	av: 337.4		

The pressure was measured by a digital Heise pressure gauge (model 710A) which was calibrated against a Budenburg dead weight tester. The pressure measurements were estimated to be accurate within ±0.014 MPa. The temperature was determined by a thermistor inserted into the top side of the view cell. The thermistor was calibrated against a Fluke digital thermometer equipped with a platinum probe (model 2180 A). The temperature measurements were estimated to be accurate within ±0.1 K. Both wet test meters were factory calibrated with a stated accuracy of 0.5%. A Sartorius balance, model 1872, was used to measure the weight of alcohol condensate collected. The weight measurements were reproducible within

0021-9568/92/1737-0337$03.00/0