Table VII. Transfer Free Energies of H^+ and Cl^- in Water-Dimethylformamide Mixtures at 25 °C on Mole Fraction Scale

wt % dimethylformamide	ΔG°_{tr}, J mol^{-1}	$\Delta G^\circ_{tr(H^+)}$, J g ion^{-1}	$\Delta G^\circ_{tr(Cl^-)}$, J g ion^{-1}
10	-864	-1400	536
20	-1371	-2900	1529
40	-3006	-9100	6094
60	-2542	-15900	13358
70	-2084	-17200	15116
80		-18400	
100		-17800	

the proton is better stabilized in the mixed solvents than in water. Thus all water-DMF mixtures including pure DMF are more basic than water. Das and Kundu (*17*) arrived at a similar conclusion and interpreted it on the basis of the good solvating nature of small cations in general and H^+ in particular by DMF through hydrogen-bonding stability in the mixed solvents and also on the more basic nature of DMF as compared to water. At the same time the hydrogen-bonding stability of Cl^- ion will decrease due to the increased anion-desolvating nature of mixed solvent. This is reflected in the increasing positive value of $\Delta G^\circ_{tr(Cl^-)}$ with the increasing proportion of DMF in the mixed solvents.

The ΔH°_{tr} values are negative throughout the composition range whereas $T\Delta S^\circ_{tr}$ values are positive upto 20 wt % of DMF and thereafter decrease, becoming increasingly negative upto 70 wt % of DMF. Franks and Ives (*25*) have emphasized the importance of these quantities in explaining the structural effects of the solvents on the transfer process. The large negative values of ΔH°_{tr} beyond 40 wt % DMF suggest the structure-making ion-solvent interactions which is also reflected in the large negative values of ΔS°_{tr} beyond 20 wt % DMF. This is also supported by the view (*26*) that all structure-forming processes, including solvation of ions, are exothermic and are accompanied by a decrease in entropy. However, the positive values of ΔS°_{tr} and the small negative values of ΔH°_{tr} upto 20 wt % DMF reflect the strong solvent-solvent interactions between water and DMF molecules in this composition region. In fact, complexes of water-DMF of the type water-$(DMF)_n$, where $n = 3$, have been reported (*27*) in this composition region, and HCl, on transfer from water to these mixtures, seems to be a better structure breaker, resulting in an increase of ΔS°_{tr}.

Registry No. HCl, 7647-01-0; H^+, 12408-02-5; Cl^-, 16887-00-6; DMF, 68-12-2; Hg, 7440-22-4; AgCl, 7783-90-6.

Literature Cited

(1) Kundu, K. K.; Chattopadyay, P. K.; Jana, D.; Das, M. N. *J. Chem. Eng. Data* **1970**, *15*, 209.
(2) Kundu, K. K.; Jana, D.; Das, M. N. *J. Chem. Eng. Data* **1974**, *19*, 329.
(3) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Chem. Soc. A*. **1971**, 1242.
(4) Kalidas, C.; Srinivas Rao, V. *J. Chem. Eng. Data* **1974**, *19*, 201.
(5) Khoo, K. H. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 554.
(6) Kalidas, C.; Sivaprasad, P. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2710.
(7) Sastry, V. V.; Kalidas, C. *J. Chem. Eng. Data* **1983**, *28*, 5.
(8) Roy, R. N.; Vernon, W.; Gibbons, J. J.; Bothwell, A. L. M. *J. Electroanal. Interfacial Electrochem.* **1972**, *34*, 101.
(9) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Electroanal. Interfacial Electrochem.* **1971**, *30*, 335.
(10) Rasmussen, S. E.; Everette, D. H. *J. Chem. Soc.* **1954**, 2812.
(11) Mussini, T.; Longhi, P.; Giammario, P. *La Chemica el Industria*, **1972**, *54*, 3.
(12) Feakins, D.; French, C. M. *J. Chem. Soc.* **1956**, 3168.
(13) Khoo, K. H. *J. Chem. Soc.* **1971**, 1177.
(14) Tayler, M. J. *J. Chem. Eng. Data* **1978**, *23*, 308.
(15) Smits, R.; Massart, D. L.; Julliard, J.; Morel, J. P. *Electrochim. Acta* **1976**, *21*, 431.
(16) Roy, R. N.; Vernon, W.; Bothwell, A. L. M. *J. Chem. Soc. B*. **1971**, 2320.
(17) Das, K. A.; Kundu, K. K. *Electrochim. Acta* **1978**, *23*, 685.
(18) Faulkner, L. R.; Bard, A. J. *J. Am. Chem. Soc.* **1968**, *90*, 6284.
(19) Geller, B. E. *Russ. J. Phys. Chem.* **1961**, *35*, 1090.
(20) Kalidas, C.; Palit, S. R. *J. Chem. Soc.* **1961**, 3998.
(21) Janz, G. J.; Ives, D. J. G. *Reference Electrodes*; Academic: New York, 1961; p 209.
(22) Hills, G. J.; Ives, D. J. G. *J. Chem. Soc.* **1951**, 308.
(23) Geller, B. E.; Ivanova, T. M. *Russ. J. Phys. Chem.* **1961**, *35*, 598.
(24) Das, K.; Kundu, K. K. *Electrochim. Acta* **1981**, *26*, 479.
(25) Franks, F.; Ives, D. J. G. *Q. Rev. Chem. Soc.* **1966**, *20*, 1.
(26) Frank, H. S.; Evans, H. G. *J. Chem. Phys.* **1945**, *13*, 507.
(27) Singh, D.; Lal Bahadur; Ramanamurthy, M. V. *J. Solution Chem.* **1977**, *6*, 703.
(28) Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*; Reinhold: New York, 1958; p 716.

Received for review May 2, 1986. Accepted October 1, 1986.

Thermodynamics of Aqueous Mixtures of Nonelectrolytes. 1. Excess Volumes of Water + γ-Butyrolactone Mixtures at Several Temperatures

Mohamoud O. Abdullah
College of Engineering, Baghdad University, Baghdad, Iraq

Suham H. F. Al-Madafi and Akl M. Awwad*
Scientific Research Council, Petroleum Research Centre, Jadiriyah, Baghdad, Iraq

Excess molar volumes of water + γ-butyrolactone mixtures were obtained from precise density measurements over the entire mole fraction range and at 10 K intervals from 288.15 to 318.15 K. Partial molar excess volumes, excess coefficients of thermal expansion, and partial molar excess expansibilities at 298.15 K were derived from the results. The significance of these results is discussed in terms of the structural changes in the mixtures.

Introduction

In our program on the thermodynamic properties of mixed solvent systems of industrial importance, we have previously studied a number of thermodynamic properties of water with *N*-methylpyrrolidone (*1*) and *N*-formylmorpholine (*2*). In this paper we report excess volumes derived from precise density measurements of water + γ-butyrolactone mixtures at 10 K intervals from 288.15 to 318.15 K. The excess coefficient of thermal expansion α^E, partial molar excess expansibilities E_i^E,

0021-9568/87/1732-0161$01.50/0 © 1987 American Chemical Society

Table I. Densities and Coefficients of Thermal Expansion for the Component Liquids

	γ-butyrolactone			
	T/K	obsd	lit.	H_2O^b
ρ/g cm^{-3}	288.15	1.13364		0.999103
	298.15	1.12436	1.1254^a	0.997048
	308.15	1.11433		0.994035
	318.15	1.10462		0.990216
$\alpha/10^3$ K^{-1}	298.15	1.7172		0.2572

[a] Reference 8. [b] Reference 9.

Table II. Molar Excess Volumes for $xH_2O + (1 - x)C_4H_6O_2$

	V_m^E/cm^3 mol^{-1}			
x	288.15 K	298.15 K	303.15 K	318.15 K
0.144 70	−0.0807	−0.0273	−0.0251	−0.0201
0.217 37	−0.1171	−0.0621	−0.0509	−0.0239
0.267 07	−0.1510	−0.0947	−0.0662	−0.0244
0.365 99	−0.2387	−0.1690	−0.1296	−0.0834
0.448 56	−0.2889	−0.2151	−0.1756	−0.1269
0.517 88	−0.3316	−0.2419	−0.1977	−0.1510
0.571 53	−0.3539	−0.2665	−0.2311	−0.1788
0.627 16	−0.3805	−0.3122	−0.2467	−0.1920
0.708 31	−0.3931	−0.3060	−0.2624	−0.2115
0.767 31	−0.4176	−0.2935	−0.2567	−0.2184
0.823 06	−0.4107	−0.2735	−0.2540	−0.2383
0.863 94	−0.3945	−0.2677	−0.2347	−0.2339
0.905 55	−0.3560	−0.2117	−0.2037	−0.2055
0.933 04	−0.2763	−0.1670	−0.1638	−0.1734
0.967 24	−0.1002	−0.0998	−0.0908	−0.0956
0.990 24	−0.0469	−0.0311	−0.0078	−0.0293

and partial molar excess volumes V_i^E are also reported.

Experimental Section

γ-Butyrolactone (Fluka AG, puriss grade) was further purified by preparative GLC using a column filled with Carbowax 20M. The final product was stored over a freshly activated molecular sieve of type 4A (Union Carbide). Analysis by the Karl Fisher method indicated the water content was usually less than 0.1% by mass in the samples used for the mixtures. Densities ρ of the samples at the four temperatures from 288.15 to 318.15 K are listed in Table I with values from the literature. These densities were extrapolated to zero water content in order to estimate the densities of pure γ-butyrolactone.

Binary mixtures of γ-butyrolactone and deionized distilled water were prepared by mass, taking into account the effect of buoyancy. A correction for the water content of the γ-butyrolactone was included in calculating mole fraction. The mole fraction error is estimated to be less than 4×10^{-5}.

Densities were determined with an Anton Paar digital densimeter (Model DMA 602) controlled ±0.001 K at each of the four operating temperatures. The uncertainties in the values of the densities are estimated to be less than 3×10^{-5} g cm^{-3}.

Results and Discussion

The experimental molar excess volumes V_m^E derived from precise density measurements for mixtures of $xH_2O + (1 - x)C_4H_6O_2$ are summarized in Table II where x represents the mole fraction of water. Some difficulty was experienced in finding a suitable smoothing equation for these results. However, the best representation was obtained with the form

$$V_m^E/\text{cm}^3\ \text{mol}^{-1} = x(1 - x)\sum_{j=1}^{k} a_j(1 - 2x)^{j-1} \qquad (1)$$

Values of the coefficients a_j and the standard deviation s at each temperature are given in Table III. Deviations of our results from their representation by eq 1 are for the most part less than 2%. However, they appear to vary systematically with mole fraction. The experimental V_m^E results are plotted against x, the mole fraction of water, in Figure 1.

Table III. Coefficients and Standard Deviations for Least-Squares Representations of Molar Excess Volumes by Eq 1

T/K	a_1	a_2	a_3	a_4	a_5	s
288.15	−1.1795	1.1607	−2.0824	1.4464	1.2994	0.0039
298.15	−0.9745	0.9897	−0.1166	0.8139	−0.406	0.0061
308.15	−0.7869	0.9058	−0.1389	0.659	−0.8694	0.0012
318.15	−0.5662	0.7381	−0.385	1.2367	−0.7489	0.0041

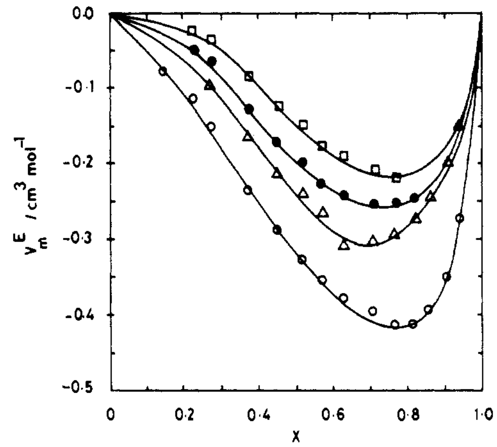

Figure 1. Plot of V_m^E against mole fraction of water: ○, 288.15; △, 298.15 K; ●, 308.15 K; □, 318.15 K.

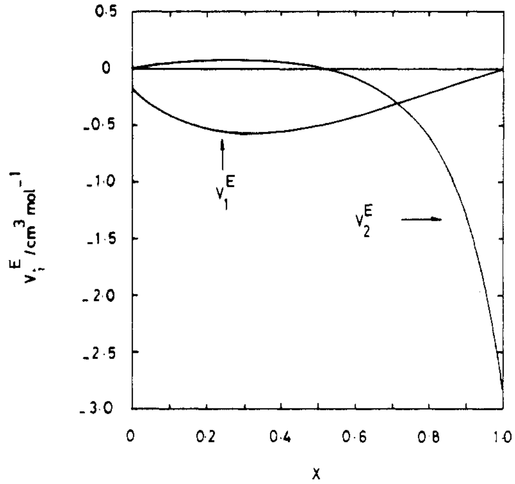

Figure 2. Plot of partial molar excess volumes V_1^E and V_2^E against mole fraction of water at 298.15 K.

The excess coefficient of thermal expansion at 298.15 K was calculated from the relation

$$\alpha^E = V_m^{-1}(\partial V_m/\partial T)_p - \sum \phi_i \alpha_i^* \qquad (2)$$

where V_m is the molar volume of the mixture, ϕ_i is the volume fraction of component i, and α_i^* is the coefficient of thermal expansion of pure component i as given in Table I.

Partial excess expansibilities at 298.15 K were calculated from the relation

$$E_i^E = (\partial V_i^E/\partial T)_p \qquad (3)$$

where V_i^E is the partial molar excess volumes obtained from the relation

$$V_i^E = V_m^E + (1 - x_i)(\partial V_m^E/\partial x_i)_{p,T} \qquad (4)$$

The calculated V_i^E, E_i^E, and α^E at 298.15 K are presented in Figures 2, 3, and 4 respectively.

The excess molar volumes, V_m^E are negative over the entire mole fraction range and temperature range (Figure 1). This

J. Chem. Eng. Data **1987**, *32*, 163-166

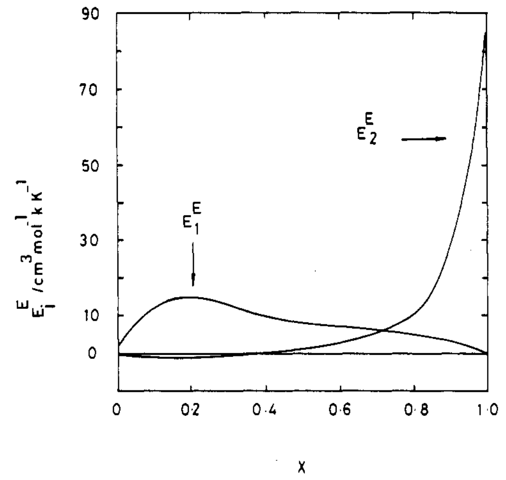

Figure 3. Partial molar excess thermal expansibilities E_1^E and E_2^E against mole fraction of water at 298.15 K.

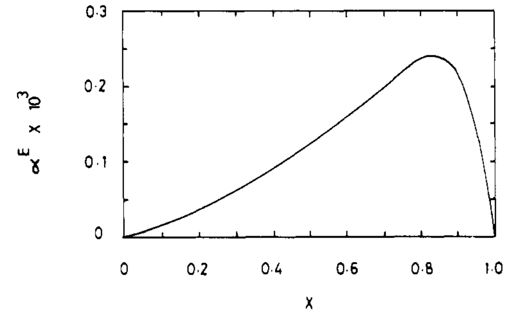

Figure 4. Coefficient of thermal expansion α^E against mole fraction of water at 298.15 K.

behavior is similar to that found (*3-6*) in aqueous mixtures with liquids such as dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and acetonitrile. The general explanation (*7*) applicable in this case, is that hydrogen bonding to the carbonyl group is stronger than to water, so that the solute enhances structure and close packing in the disordered regions.

Excess partial molar volumes are illustrated in Figure 2. It is interesting that the largest negative V_2^E occurs at a lower mole fraction of γ-butyrolactone, but that with further addition of γ-butyrolactone V_2^E decreases rapidly until about $x = 0.6$ and then gradually approaches its ideal value. This suggests that larger amounts of γ-butyrolactone disrupt the structure and thereby V_2^E decrease.

It may observed that on addition of γ-butyrolactone the E_i^E (Figure 3) and α^E (Figure 4) show that close packing is a maximum at low mole fraction of γ-butyrolactone ($x \leq 0.2$) as expected from thermal disruption of the water ice I structure.

Glossary

a_1, a_2, a_j	coefficients in representation of excess molar volume by eq 1
E_i^E	partial molar excess expansibilities
k	number of coefficients in eq 1
s	standard deviation
T	thermodynamic temperature, K
V_m^E	molar excess volume, cm^3 mol^{-1}
V_i^E	excess partial molar volume
V_m	molar volume of the mixture
x	mole fraction of water

Greek Letters

α_1^*	thermal expansion coefficient of pure water
α^E	excess thermal expansion coefficient
ϕ_1	volume fraction of pure water

Registry No. γ-Butyrolactone, 96-48-0.

Literature Cited

(1) Kanbour, F.; Awwad, A. M. *Iraqi J. Sci.* **1980**, *21*, 693.
(2) Awwad, A. M.; North, A. M.; Pethrick, R. A. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 449.
(3) de Visser, C.; Perron, G.; Desnoyers, J. G.; Heuvesland, W. J.; Somsen, G. *J. Chem. Eng. Data* **1977**, *22*, 74.
(4) Kiyohara, O.; Perron, G.; Desnoyers, J. G. *Can. J. Chem.* **1975**, *53*, 3263.
(5) Kiyohara, O.; D'Acrey, P. J.; Benson, G. C. *Can. J. Chem.* **1978**, *56*, 2803.
(6) Handa, Y. P.; Benson, G. C. *J. Solution Chem.* **1981**, *10*, 291.
(7) Petersen, R. C. *J. Phys. Chem.* **1960**, *64*, 184.
(8) Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1965; Vol. II.
(9) Kell, G. S. *J. Phys. Chem. Ref. Data* **1977**, *6*, 1109.

Received for review January 28, 1986. Accepted October 6, 1986.

PVT Measurements on Benzene at Temperatures to 723 K

Gerald C. Straty,* Martin J. Ball, and Thomas J. Bruno

Thermophysics Division, Center for Chemical Engineering, National Bureau of Standards, Boulder, Colorado 80303

Measurements of the *PVT* behavior of compressed gaseous and liquid benzene are reported. Pressure vs. temperature observations were made along paths of very nearly constant density (pseudoisochores) in the temperature range from about 425 K to over 720 K and at pressures to about 35 MPa. Twenty-four pseudoisochores were determined ranging in density from about 1 mol/dm^3 to over 9 mol/dm^3.

Introduction

Although *PVT* data for benzene are available from a number of sources (*1-5*), data remain scarce at elevated temperatures, particularly above the critical temperature. The *P-T* loci of the principal benzene data are shown in Figure 1. Only the data of Gehrig and Lentz (*4*) and Gornowski et al. (*3*) are available above about 590 K, and those of ref *3* are limited to low densities. We report new measurements of the *PVT* behavior of compressed gaseous and liquid benzene in the temperature range from about 425 K to over 720 K at pressures to about 35 MPa. Pressure vs. temperature observations were made along paths of nearly constant density (pseudoisochores). Twenty-four pseudoisochores were determined ranging in density from about 1 mol/dm^3 to 9 mol/dm^3.

Experiment

Measurements were made using an automated high-temperature *PVT* apparatus which has been described in detail (*6*).