Table VII. Enthalpy of Solution of $NH_4 \cdot 1.1758CO(NH_2)_2$[a] in Water at 25 °C

% N	molality of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$, m_t (eq 8)	ΔH, cal/g
2	0.3452	67.29
4	0.7283	65.82
6	1.1558	64.25
8	1.6360	62.60
10	2.1793	60.85
12	2.7990	59.00
14	3.5123	57.08
16	4.3423	55.08
18	5.3202	53.05
20	6.4893	51.02
22	7.9117	49.08
24	9.6798	47.33
26	11.9372	45.91
28	14.9193	44.79
30	19.0422	43.18
32	25.1151	36.18

[a] $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$ = 53.13% NH_4NO_3 and 46.87% $CO(NH_2)_2$.

$aCO(NH_2)_2$ is considered as the solute and water as the solvent, the solution can be described in molality $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$, m_t, since $a = 1.1758$. The determinations of the integral enthalpy of solution for the three values of m_t are described in Table V.

The integral enthalpies of solution for the solutions listed in Table IV were calculated using eq 7 where ΔH_I is the integral

$$\Delta H_I = \Delta H_F - \Delta H_D \tag{7}$$

enthalpy of solution of the initial solution, ΔH_F is the integral enthalpy of solution of the final solution, and ΔH_D is the enthalpy of dilution. A weighed amount of the solution was diluted with a weighed amount of water in the solution calorimeter and ΔH_D in cal/mol of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$ was measured. The enthalpy, ΔH_F, for each measurement was calculated from an equation of ΔH_4 as a function of m_t over the concentration range covered by the enthalpy of solution measurements listed in Table V. The observed enthalpies of dilution and the integral enthalpies of solution calculated from them are listed in Table VI.

The values of m_t and the average values of ΔH_I from Table VI were combined with the values for m_t and ΔH_4 from Table V, and eq 8, where ΔH is the integral enthalpy of solution in

$$\Delta H = 10.35 - 0.6205m_t + 0.03782m_t^2 - 0.0008313m_t^3 \tag{8}$$

kcal/mol of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$, was fitted to the observed values by the "least-squares" method with a standard deviation of 0.06 kcal/mol.

Table VII lists the enthalpies of solution of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$ in calories per gram to form solutions of various nitrogen concentrations. They were determined by solving eq 8 for values of m_t corresponding to the nitrogen concentrations and dividing by 150.657 12, the gram formula weight of $NH_4NO_3 \cdot 1.1758CO(NH_2)_2$.

Literature Cited

(1) Egan, E. P., Jr.; Luff, B. B. *J. Chem. Eng. Data* **1966**, *11*, 192.
(2) Johnson, F. J.; Miller, D. L. *J. Assoc. Off. Anal. Chem.* **1974**, *57*, 8.
(3) Johnson, F. J.; Woodis, T. C., Jr.; Cummings, J. M., Jr. *J. Assoc. Off. Anal. Chem.* **1974**, *57*, 10.
(4) Luff, B. B.; Reed, R. B.; Wakefield, Z. T. *J. Chem. Eng. Data* **1972**, *17*, 96.
(5) *Natl. Bur. Stand. (U.S.), Tech. Note* **1968**, *No. 270-3*.

Received for review September 5, 1978. Accepted February 10, 1979.

Volume Changes on Mixing 1,4-Dioxane with Cyclopentane, Pentane, and 2-Methylbutane

Miguel A. Leiva, Jerry P. Greenberg, and Charles M. Knobler*
Department of Chemistry, University of California, Los Angeles, California 90024

Measurements are reported of the excess volumes for 1,4-dioxane + *n*-pentane at 25 °C and for 1,4-dioxane + cyclopentane and 1,4-dioxane + 2-methylbutane at 20 °C. The excess volume V_m^E is positive and nearly symmetric in mole fraction for the cyclopentane mixture but changes from positive to negative with increasing mole fraction of dioxane in the other two systems. Similar variations in V_m^E with degree of branching have been observed in mixtures of C_6-alkanes with 1,4-dioxane, nitroethane, and 1-chloropentane.

Measurements at 40 °C of the excess volumes, V_m^E, for binary liquid mixtures of nitroethane with hexane isomers and with cyclohexane (*1*, *2*) show a striking dependence on the number of methyl groups in the hexane. For the mixture with cyclohexane, V_m^E is positive and nearly symmetric in mole fraction. As the number of methyl groups in the hexane is increased, the excess volume becomes increasingly smaller and skewed, eventually changing from positive to negative with increasing mole fraction of nitroethane in the 2-methylpentane system. The excess volume for the 2,2-dimethylbutane mixture changes from positive to negative at about 0.2 mol fraction nitroethane.

Similar trends have been observed in mixtures of hexanes with 1,4-dioxane (*2*) and with 1-chloropentane (*3*), strengthening the supposition that they reflect the properties of the hexane. Mixtures of hexanes with hexadecane also display a trend toward increasingly negative volume changes (*4*), but there is no accompanying change in the shape of the V_m^E vs. mole fraction curve. A recent study of cyclohexane + hexadecane (*5*) demonstrates that the V_m^E is positive.

No completely satisfactory explanation of these trends has been put forward. In an effort to gain more insight into the problem, we are investigating volume changes in related systems. We report here results for binary mixtures of 1,4-dioxane with cyclopentane, *n*-pentane, and 2-methylbutane.

Experimental Section

Volume Change Measurements. Details of the measurements, which were made with a continuous dilution dilatometer,

0021-9568/79/1724-0208$01.00/0

Table I. Excess Volumes, V_m^E

x	V_m^E/cm^3 mol^{-1}	x	V_m^E/cm^3 mol^{-1}
n-Pentane + 1,4-Dioxane at 25 °C			
0.0394	0.073	0.5100	0.054
0.0705	0.115	0.5615	0.037
0.1498	0.177	0.5638	0.029
0.2232	0.178	0.5998	0.019
0.3262	0.155	0.6531	−0.002
0.3624	0.137	0.6809	−0.012
0.4527	0.093	0.7793	−0.044
0.4691	0.073	0.9332	−0.039
0.4816	0.078	0.9795	−0.026
2-Methylbutane + 1,4-Dioxane at 20 °C			
0.0096	0.006	0.5344	−0.169
0.0184	0.015	0.6100	−0.185
0.0242	0.020	0.6155	−0.188
0.0319	0.026	0.6493	−0.193
0.0568	0.039	0.6629	−0.195
0.0768	0.045	0.6839	−0.193
0.1362	0.046	0.7108	−0.194
0.1463	0.041	0.7377	−0.191
0.1786	0.030	0.7667	−0.185
0.2115	0.014	0.7911	−0.176
0.2511	−0.006	0.8254	−0.161
0.2859	−0.027	0.8536	−0.143
0.3180	−0.047	0.8894	−0.120
0.3472	−0.066	0.9181	−0.097
0.3711	−0.081	0.9431	−0.069
0.4103	−0.103	0.9681	−0.039
0.4445	−0.124	0.9858	−0.019
0.4757	−0.153	0.9927	−0.010
Cyclopentane + 1,4-Dioxane at 20 °C			
0.0094	0.038	0.4579	0.614
0.0177	0.070	0.4743	0.609
0.0261	0.100	0.4843	0.610
0.0598	0.208	0.5551	0.568
0.0885	0.290	0.5684	0.557
0.1237	0.372	0.5813	0.550
0.1615	0.443	0.6058	0.532
0.1897	0.487	0.6267	0.514
0.2139	0.519	0.6475	0.494
0.2478	0.554	0.6709	0.471
0.2749	0.561	0.6943	0.446
0.2974	0.592	0.7192	0.417
0.3159	0.601	0.7196	0.417
0.3275	0.607	0.7465	0.383
0.3426	0.613	0.7828	0.342
0.3603	0.618	0.8146	0.293
0.3605	0.617	0.8454	0.249
0.3775	0.620	0.8865	0.187
0.3932	0.622	0.9249	0.126
0.4056	0.621	0.9587	0.070
0.4125	0.620	0.9812	0.032
0.4240	0.621	0.9908	0.016
0.4377	0.619		

are described elsewhere (*4*). In order to cover the entire mole fraction range, two dilution runs were made for each system. The temperature was measured with a Beckmann thermometer calibrated against the 25-Ω platinum resistance thermometer used in the previous studies. Densities of the hydrocarbons were taken from the API tables (*6*); the density of the dioxane was measured with a Mettler-Paar digital density meter.

Materials. Cyclopentane, *n*-pentane, and 2-methylbutane with reported minimum purities of 98, 99+, and 99+ mol %, respectively, were obtained from Matheson Coleman and Bell and were used without further purification. Malinckrodt 1,4-dioxane was purified as described by Handa et al. (*3*). Its density at 20 °C was 1.033 75 g cm^{-3}. Prior to use, the samples were dried over freshly activated molecular sieve (Union Carbide Type 4A) and degassed by vacuum sublimation (*7*) and stored in mercury-sealed bulbs.

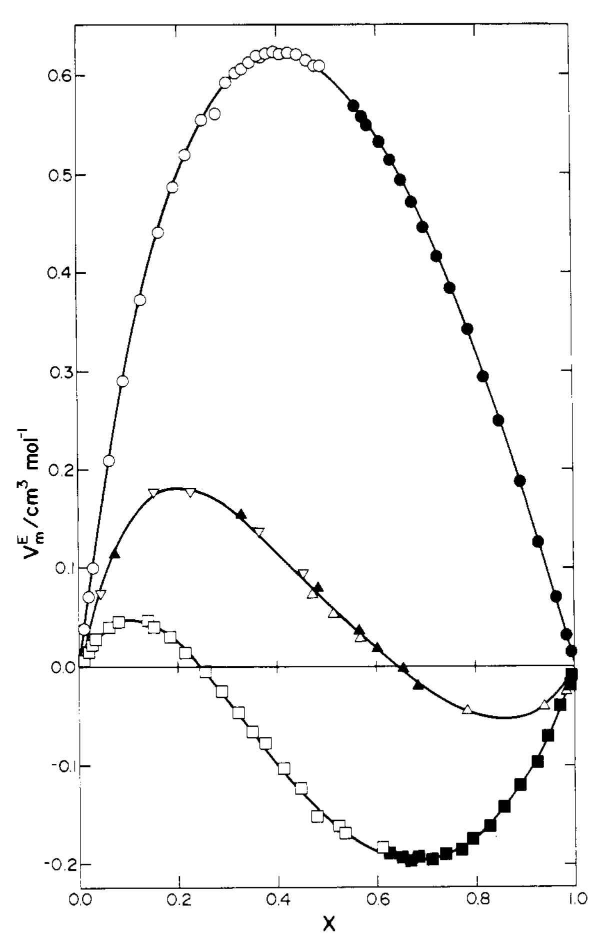

Figure 1. Excess volumes. Open, closed, and inverted symbols represent different dilution runs: upper curve, cyclopentane + 1,4-dioxane at 20 °C; middle curve, *n*-pentane + 1,4-dioxane at 25 °C; lower curve, 2-methylbutane + 1,4-dioxane at 20 °C.

Results and Discussion

The system *n*-pentane + 1,4-dioxane was investigated at 25 °C; cyclopentane + 1,4-dioxane and 2-methylbutane + 1,4-dioxane were studied at 20 °C. Experimentally determined excess volumes are given in Table I and are plotted in Figure 1.

A smoothing equation of the form

$$V_m^E/\text{cm}^3\ \text{mol}^{-1} = x(1-x)[v_0 + v_1(1-2x) + v_2(1-2x)^2 + v_3(1-2x)^3]$$

where x refers to the mole fraction of dioxane, was fitted to the data. Values of the parameters v_0, v_1, v_2, and v_3, their respective standard deviations, and the standard deviations for the excess volumes are given in Table II.

Table II. Parameters in the Smoothing Equation, Their Respective Standard Deviations, and Standard Deviations for Excess Volumes, $\sigma(V_m^E)$

system	v_0	$\sigma(v_0)$	v_1	$\sigma(v_1)$	v_2	$\sigma(v_2)$	v_3	$\sigma(v_3)$	$\sigma(V_m^E)$/cm^3 mol^{-1}
cyclopentane + 1,4-dioxane	2.393	0.003	0.863	0.012	0.431	0.017	0.295	0.034	0.0030
n-pentane + 1,4-dioxane	0.261	0.007	1.002	0.033	0.438	0.045	0.552	0.090	0.0049
2-methylbutane + 1,4-dioxane	−0.614	0.003	0.890	0.011	0.404	0.014	0.324	0.029	0.0025

The changes in V_m^E with increasing number of methyl groups in the hydrocarbon parallel those observed in mixtures with the hexanes. Although the n-pentane mixture has been studied at a higher temperature than the other two systems, its characteristics would not be expected to change appreciably in 5 °C (*1*).

Literature Cited

(1) Reeder, J., Block, T. E., Knobler, C. M., *J. Chem. Thermodyn.*, **8**, 133 (1976).
(2) Andrews, A. W., Morcom, K. W., *J. Chem. Thermodyn.*, **3**, 513 (1971).
(3) Handa, Y. P., Knobler, C. M., Scott, R. L., *J. Chem. Thermodyn.*, **9**, 451 (1977).
(4) Reeder, J., Knobler, C. M., Scott, R. L., *J. Chem. Thermodyn.*, **7**, 345 (1975).
(5) Reeder, J., Knobler, C. M., Scott, R. L., unpublished data.
(6) Rossini, F. D., Ed., *Am. Pet. Inst.*, Project 44 Tables (1953).
(7) Bell, T. N., Cussler, E. L., Harris, K. R., Pepela, C. N., Dunlop, P. L., *J. Phys. Chem.*, **72**, 4693 (1968).

Received for review August 17, 1978. Accepted February 10, 1979. Acknowledgment is made to the National Science Foundation for support of this research. M.A.L. was the recipient of a grant given jointly by the CONACYT, Universidad Autonoma Metropolitana, and the Mexican National Council for Science and Technology.

Osmotic and Activity Coefficients of Lithium Chlorate and Lithium Bromate

Oscar D. Bonner

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Osmotic and activity coefficients are reported for solutions of lithium chlorate and lithium bromate. It is demonstrated that the coefficients of the lithium, sodium, and potassium chlorates, bromates, and iodates have the expected relationship one to another.

The osmotic and activity coefficients of many of the simple uni-univalent electrolytes are available in the literature. Some of the electrolytes have not been studied, however, because of lack of a direct use for the data or because of the difficulties in handling. We had had occasion to measure the coefficients for the lithium (*1*), sodium (*2*), and potassium (*1*) iodates. Data for the sodium and potassium chlorates and bromates are available (*3*) elsewhere in the literature. It seemed that the completion of the families by measurement of the coefficients of the lithium chlorate and bromate would be of interest in that a quantitative pattern could be established for the variation of the coefficients with ion size and polarizability.

Method

Lithium chlorate and bromate may be purchased from Pfaltz and Bauer but the purity of the product is not specified. Lithium chlorate is particularly difficult to purify and handle as the solid because of its deliquescent nature. It was decided to obtain solutions of the lithium salts rather than to attempt to weigh accurate amounts of the solids. Consequently, solutions of reagent grade sodium salts were passed through a cation-exchange column which had been converted to the lithium form. The concentrations of the effluent solutions were determined by passing measured quantities through a second ion-exchange column in the acid form and subsequent titration. This method has been used to determine molecular weights of salts which agree with the calculated formula weight within 0.1% (*4*). It is believed that the error in the osmotic coefficients caused by the uncertainty in the solution concentration does not exceed 0.2%.

The isopiestic equilibration of solutions of these salts and solutions of sodium chloride was performed in the usual manner. It was established that equilibrium was reached when the concentrations of identical samples were within 0.1% agreement, with one sample losing weight and the other gaining weight to attain equilibrium. The equilibration time varied from 24 h for the most concentrated solutions to about 10 days for the most dilute. An additional check on the accuracy of the data is the coincidence of molality ratio curves from different experiments.

Table I. Molalities of Isopiestic Solutions

NaCl	$LiClO_3$	$LiBrO_3$
0.2782	0.2719	0.2779
0.5335	0.5111	0.5319
0.819	0.769	0.815
1.011	0.931	1.002
1.221	1.114	1.209
1.475	1.329	1.456
1.817	1.612	1.785
2.195	1.925	2.155
2.455	2.141	2.412
3.207	2.753	3.144
3.591	3.057	3.519
4.022	3.414	3.945
4.486	3.797	4.398
5.022	4.226	4.925

Table II. Osmotic and Activity Coefficients at 25 °C

	$LiClO_3$		$LiBrO_3$	
m	ϕ	γ	ϕ	γ
0.1	0.939	0.790	0.932	0.778
0.2	0.941	0.758	0.926	0.735
0.3	0.945	0.742	0.924	0.711
0.4	0.951	0.735	0.922	0.694
0.5	0.961	0.736	0.924	0.684
0.6	0.971	0.739	0.927	0.677
0.7	0.983	0.745	0.930	0.672
0.8	0.994	0.752	0.934	0.668
0.9	1.008	0.762	0.938	0.666
1.0	1.020	0.772	0.943	0.666
1.2	1.044	0.796	0.953	0.666
1.4	1.069	0.825	0.964	0.669
1.6	1.094	0.855	0.976	0.675
1.8	1.112	0.886	0.990	0.683
2.0	1.142	0.921	1.003	0.691
2.5	1.203	1.018	1.035	0.718
3.0	1.267	1.130	1.070	0.749
3.5	1.326	1.254	1.107	0.788
4.0	1.384	1.394	1.144	0.832
4.2	1.408	1.454		
4.5			1.183	0.883
5.0			1.223	0.938

0021-9568/79/1724-0210$01.00/0