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Thermodynamics of Aqueous Mixed Potassium Carbonate, Bicarbonate, and Chloride Solutions to 368 K

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Potentials for the cell without liquid junction $H_2,Pt|K_2CO_3(m_1),KHCO_3(m_2),KCl(m_3)|AgCl,Ag$ are reported over a wide range of ionic strengths at temperatures to 368.15 K. Analysis of these results with the ion interaction model shows that only very minor changes in the previously reported temperature dependence of the potassium carbonate interaction parameters are required to represent the higher temperature data. Activity and osmotic coefficients for solutions with stoichiometrically equal carbonate and bicarbonate molalities are calculated from 338 to 368 K.

Introduction

Previous reports of the thermodynamic properties of aqueous mixed electrolyte solutions (*1*, *2*) containing carbonate and bicarbonate have been concerned with values in the 278–318 K temperature range. Application of the ion interaction model for mixed electrolytes to the experimental results in this temperature region has made available a straightforward method of calculating excess thermodynamic properties under these conditions.

The present study was undertaken to determine values of thermodynamic properties of carbonate solutions in the temperature range 338–368 K. In addition, it is of interest to investigate the behavior of the ion interaction parameters for this system at temperatures above those studied earlier.

A complicating factor in the analysis of the results for the carbonate solutions is the presence of the hydrolysis and disproportionation equilibria

$$CO_3^{2-}(aq) + H_2O(l) = HCO_3^-(aq) + OH^-(aq)$$

$$2HCO_3^-(aq) = CO_3^{2-} + CO_2(g) + H_2O(l) \qquad (1)$$

These reactions make it necessary to treat experimental results for even stoichiometrically single solute systems with a model appropriate for mixed electrolyte solutions. Also, as the results reported here do not extend to very low carbonate concentrations, values of the first and second ionization constants for carbonic acid and the solubility of $CO_2(g)$ in aqueous electrolyte must be taken from independent experimental determinations.

In this work, we have measured potentials for the cell without liquid junction

$$Pt,H_2|K_2CO_3(m_1),KHCO_3(m_2),KCl(m_3)|AgCl,Ag \qquad (I)$$

with reaction

$$\tfrac{1}{2}H_2(g) + AgCl(s) + CO_3^{2-}(aq) = Cl^-(aq) + HCO_3^-(aq) + Ag(s) \qquad (2)$$

Analysis of these results allows us to calculate excess thermodynamic properties for mixed potassium (carbonate + bicarbonate) solutions to 368 K.

Experimental Section

Salts used in this work were all ACS-certified grade (Fisher). The potassium chloride was dried prior to use; other salts were used as received. Solutions for each cell were prepared by weighing the solid salts individually and dissolving them in CO_2-free doubly distilled water. Vacuum corrections were applied to all weighings. Uncertainties in calculated molalities due to weighing imprecision were within ±0.04 %.

Cell potentials were measured with a Keithley Model 191 digital multimeter. The Ag–AgCl electrodes were of the thermal electrolytic type (*3*), with bias potentials always better than ±0.05 mV. Detailed experimental procedures for hydrogen electrode preparation, Ag–AgCl electrode preparation, cell filling, and temperature control have been given elsewhere (*4*, *5*).

Dissolved oxygen was removed by purging the cells with hydrogen gas (purified with two De-Oxo catalysts coupled in series) for about 30 min. Temperature control of the oil bath thermostat was better than ±0.1 K. Cell potentials were usually determined at 338.15 K first, followed by measurements at 348.15 K. Fresh solutions and new electrodes were used in subsequent runs at 358.15 and 368.15 K. Observed potentials were stable within ±0.4 mV at the highest temperature, with smaller instabilities noted at lower temperatures. Slight drifts were noted in some runs at high ionic strength at 368.15 K.

Results

Stoichiometric molalities, experimental temperatures, and barometric pressures, and observed (uncorrected) cell potentials are listed in Table I. The solution compositions range from 0.2 to 6.3 mol·kg^{-1} ionic strength; the relatively high lower concentration limit implies that these results will not contribute to our knowledge of pK_2 at these temperatures. Experimental difficulties encountered in this elevated-temperature work, including uncertain temperature equilibration, silver chloride solubility, and possible composition changes due to incomplete gas presaturation, result in greater uncertainty in measured potentials than in earlier work with these cells at lower temperatures (*1*). We note also that some of the sources of error (e.g., AgCl solubility) may lead to systematic deviations of a given set of runs at a particular temperature. The results reported in Table I include values which are not in good agreement with other results of this study at similar experimental conditions. These values, noted in Table I, were not included in the analysis described below. Differences between observed potentials and those calculated with the treatment below are shown for the excluded data in Figures 1 and 2. Where a number of potentials measured at a single temperature in a particular run showed large deviations, that set was excluded from the analysis.

Observed potentials for cell I may be written as

$$E = E^\circ(AgCl,Ag) - (RT/F)\{\ln\,[K_2(p_0/f_{H_2})^{1/2}] + \ln\,(m_{Cl}m_{HCO_3}/m_{CO_3}m_0) + \ln\,(\gamma_{Cl}\gamma_{HCO_3}/\gamma_{CO_3})\} \qquad (3)$$

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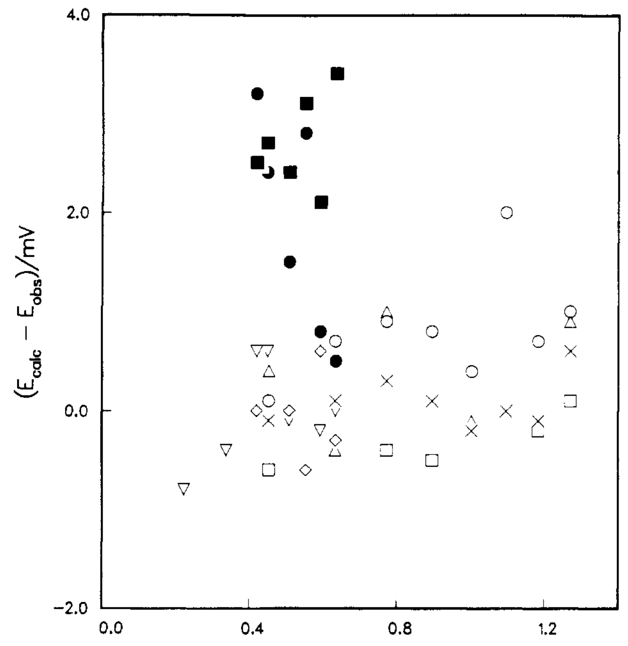

Figure 1. Differences in observed and calculated potentials for (run 1, run 2) plotted against the square root of the stoichiometric ionic strength at (■, ○), 338.15 K; (●, ×), 348.15 K; (◇, △), 358.15 K; (▽, □), 368.15 K.

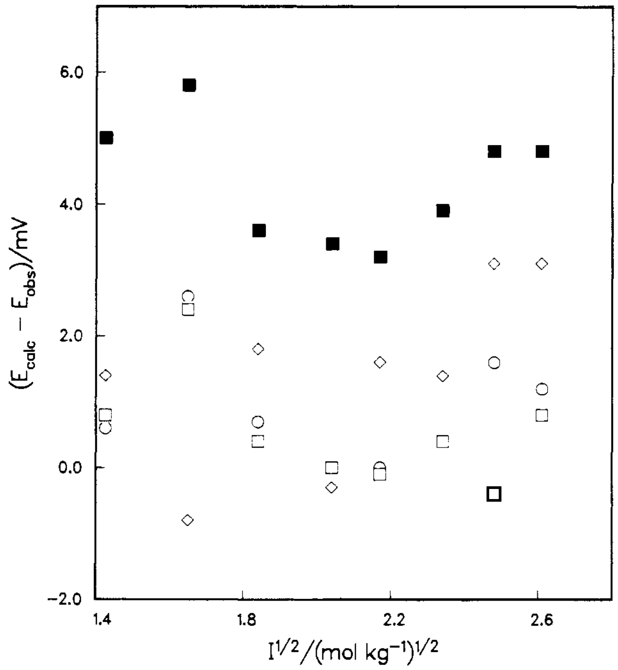

Figure 2. Differences in observed and calculated potentials from run 4 plotted against the square root of the stoichiometric ionic strength at □, 338.15 K; ○, 348.15 K; ■, 358.15 K; ◇, 368.15 K.

where K_2 is the second dissociation constant of carbonic acid, f_{H_2} is the fugacity of hydrogen gas, p_0 = 101.325 kPa, and m_0 = 1.0 mol·kg^{-1}. The symbols R, T, and F retain their usual meanings; values of R and F are taken from Cohen and Taylor (*6*). Standard electrode potentials $E°$(AgCl,Ag) were calculated from the values given by Bates (*3*) and the measured constant offset (0.000 25 V) between Bates' tabulated values and those determined for the electrodes used in this work. This calculation gives standard potentials of 0.192 50, 0.1835, 0.1774, and 0.1635 V at 338.15, 348.15, 358.15, and 368.15 K.

We have used the ion interaction treatment developed for mixed strong electrolytes by Pitzer and Kim (*7*) to represent the activity coefficients as functions of temperature and solution composition. The quantity to be expressed in this treatment is the logarithm of the activity coefficient ratio in eq 3. The ion interaction expression for this quantity is

$$\begin{aligned}\ln(\gamma_{HCO_3}\gamma_{Cl}/\gamma_{CO_3}) = {} & 2A_\varphi\{I^{1/2}/(1 + bI^{1/2}) + \\ & (2/b)\ln(1 + bI^{1/2})\} + 2m_K(B_{K,HCO_3} + B_{K,Cl} - B_{K,CO_3}) + \\ & 2m_K{}^2(C_{K,HCO_3} + C_{K,Cl} - C_{K,CO_3}) - 2m_K(m_{CO_3}B'_{K,CO_3} + \\ & m_{HCO_3}B'_{K,HCO_3} + m_{OH}B'_{K,OH} + m_{Cl}B'_{K,Cl}) + 2m_{CO_3} \times \\ & (\Theta_{CO_3,HCO_3} + \Theta_{CO_3,Cl}) + m_Km_{CO_3}(\psi_{K,CO_3,HCO_3} + \psi_{K,CO_3,Cl}) + \\ & 2m_{HCO_3}(\Theta_{HCO_3,Cl} - \Theta_{CO_3,HCO_3}) + m_Km_{HCO_3}(\psi_{K,HCO_3,Cl} - \\ & \psi_{K,CO_3,HCO_3}) + 2m_{OH}(\Theta_{HCO_3,OH} + \Theta_{OH,Cl} - \Theta_{CO_3,OH}) + \\ & m_Km_{OH}(\psi_{K,HCO_3,OH} + \psi_{K,Cl,OH} - \psi_{K,CO_3,OH}) + \\ & 2m_{Cl}(\Theta_{HCO_3,Cl} - \Theta_{CO_3,Cl}) + m_Km_{Cl}(\psi_{K,HCO_3,Cl} - \psi_{K,CO_3,Cl}) - \\ & 2m_{CO_3}(m_{HCO_3} + m_{OH} + m_{Cl})({}^E\Theta'_{2,1}) \end{aligned} \quad (4)$$

The second and third virial coefficients $B_{c,a}$ and $C_{c,a}$ are defined in terms of the adjustable parameters $\beta^{(0)}_{c,a}$, $\beta^{(1)}_{c,a}$, and $C^{\varphi}_{c,a}$ as

$$B_{c,a} = \beta^{(0)}_{c,a} + \beta^{(1)}_{c,a}(2/\alpha^2 I)\{1 - (1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})\} \quad (5)$$

$$C_{c,a} = C^{\varphi}_{c,a}/(2|Z_cZ_a|^{1/2}) \quad (6)$$

Also

$$B'_{c,a} = \beta^{(1)}_{c,a}(2/\alpha^2 I^2)\{-1 + (1 + \alpha I^{1/2} + \tfrac{1}{2}\alpha^2 I)\exp(-\alpha I^{1/2})\} \quad (7)$$

The parameters b and α have values 1.2 kg$^{1/2}$·mol$^{-1/2}$ and 2.0 kg$^{1/2}$·mol$^{-1/2}$, respectively. I is the solution ionic strength. The limiting slope A_φ was calculated from the dielectric constant equation of Bradley and Pitzer (*8*) and the equation of state for water of Haar, Gallagher, and Kell (*9*, *10*).

Higher order electrostatic effects contribute to the mixing coefficients $\Theta_{i,j}$ when ions i and j have different charge numbers. These effects have been described in detail by Pitzer (*11*, *12*). Unsymmetrical mixing coefficients have the form

$$\Theta_{i,j} = {}^S\Theta_{i,j} + {}^E\Theta_{i,j} \quad (8)$$

where ${}^S\Theta_{i,j}$ is evaluated empirically and ${}^E\Theta_{i,j}$ is the calculated higher order electrostatic contribution. We use the full electrostatic mixing treatment here, with the integral approximation functions given in ref *11* used to reduce the calculation time required.

The hydrolysis and disproportionation equilibria (eq 1) complicate the application of the ion interaction treatment to these results. The fitting procedure is iterative; activity coefficients are calculated from assumed parameter values and stoichiometric molalities, equilibrium molalities are calculated, and revised parameter values are obtained through least-squares regression. The procedure is repeated to convergence of the optimized parameters.

A further complication in handling these data is the required correction to constant hydrogen fugacity. At these higher temperatures, the vapor pressure of water contributes significantly to the total pressure over the solutions, and corrections to the hydrogen fugacity are significant. These corrections are included in the iterative calculations. The activity of water is calculated for each solution, and hydrogen fugacity corrections are made based on calculated water activities and observed barometric pressures.

Values of the first and second dissociation constants for carbonic acid were calculated from the equations given by Patterson, Slocum, Busey, and Mesmer (*13*) and Patterson, Busey and Mesmer (*14*), respectively. These values of K_1 and K_2 are in good agreement with those calculated from the equations given by Peiper and Pitzer (*2*) from 278 to 318 K.

Table I. Measured Cell Potentials and Solution Molalities $m_1(K_2CO_3)$, $m_2(KHCO_3)$, $m_3(KCl)$

Run 1								
m_1/(mol·kg^{-1})	0.01002	0.02137	0.03061	0.03973	0.04966	0.05816	0.06968	0.08047
m_2/(mol·kg^{-1})	0.00956	0.02744	0.03105	0.04207	0.04815	0.06038	0.07018	0.07979
m_3/(mol·kg^{-1})	0.01003	0.02179	0.05274	0.04009	0.06060	0.07000	0.07083	0.08054
E/V at								
338.15 K, 96.71 kPa^a	0.97137^b	0.94463^b	0.93733	0.93100	0.92728	0.92090	0.91973	0.91442
348.15 K, 96.68 kPa^a	0.97480^b	0.95089^b	0.94367	0.93712	0.93375	0.92801	0.92590	0.92059
358.15 K, 96.68 kPa^a	0.97700^b	0.95358^b	0.94727	0.94028^b	0.93692	0.93165	0.92922	0.92481
368.15 K, 96.57 kPa	0.98987	0.96088	0.93756	0.94582	0.93528	0.92890	0.92893	0.92470
Run 2								
m_1/(mol·kg^{-1})	0.03987	0.08003	0.11971	0.16018	0.20014	0.24031	0.28000	0.32000
m_2/(mol·kg^{-1})	0.04075	0.07977	0.12063	0.15933	0.20281	0.23960	0.27966	0.32132
m_3/(mol·kg^{-1})	0.04400	0.08021	0.11958	0.16144	0.20122	0.24111	0.28092	0.33250
E/V at								
338.15 K, 96.71 kPa	0.93842	0.91846	0.90461	0.89488	0.88729	0.87987	0.87583	0.86964
348.15 K, 96.71 kPa	0.94644	0.92650	0.91288	0.90238	0.89433	0.88818	0.88269	0.87586
358.15 K, 96.61 kPa	0.95385	0.93473	0.91895		0.90109		0.88922	0.88194
368.15 K, 96.61 kPa	0.94494	0.92501	0.91073	0.90053			0.87989	0.87338
Run 3								
m_1/(mol·kg^{-1})	0.05950	0.35942	0.43074	0.47890	0.23954	0.17837	0.12177	0.29980
m_2/(mol·kg^{-1})	0.18027	1.0812	1.2584	1.4449	0.72079	0.53779	0.36381	0.90155
m_3/(mol·kg^{-1})	0.06881	0.33850	0.73010	0.47284	0.24038	0.18131	0.12131	0.30290
E/V at								
338.15 K, 96.51 kPa	0.89089	0.83496	0.81170	0.82466		0.85820	0.87243	0.84090
348.15 K, 96.51 kPa	0.89770	0.83923	0.81665	0.82816		0.86321	0.87389	0.84537
358.15 K, 96.51 kPa	0.90515	0.84482	0.82151	0.83343			0.88450	0.85072
368.15 K, 96.55 kPa	0.89529	0.83559	0.81204			0.86090	0.87458	0.84137
Run 4								
m_1/(mol·kg^{-1})	0.15834	0.32970	0.46134	0.62426	0.78124	0.95494	1.1143	1.2683
m_2/(mol·kg^{-1})	0.16696	0.31801	0.45772	0.63997	0.78309	0.95976	1.1297	1.2619
m_3/(mol·kg^{-1})	0.17834	0.31732	0.46136	0.67426	0.78192	0.95976	1.1297	1.2619
E/V at								
338.15 K, 96.02 kPa		0.87242		0.84667	0.84190	0.83584	0.83202	0.82852
348.15 K, 96.02 kPa		0.87818		0.85135	0.84754	0.84082	0.83655	0.83309
358.15 K, 96.02 kPa				0.85407	0.85143	0.84356	0.83989	0.83661
368.15 K, 96.02 kPa	0.89561	0.87569	0.86033	0.84558	0.84383	0.83713		0.82679
Run 5								
m_1/(mol·kg^{-1})	0.55445	0.74630	0.91680	1.1223	1.2759	1.4915	1.6758	1.8534
m_2/(mol·kg^{-1})	0.18331	0.24948	0.30640	0.41046	0.45717	0.49803	0.56278	0.62216
m_3/(mol·kg^{-1})	0.18620	0.24244	0.31513	0.37733	0.43849	0.49924	0.55134	0.62554
E/V at								
338.15 K, 97.13 kPa	0.91941	0.90899	0.90263	0.89510	0.89169	0.89015	0.88720	0.88493
348.15 K, 97.13 kPa	0.92683	0.91537	0.90875	0.90113	0.89736	0.89581	0.89221	0.88981
358.15 K, 97.13 kPa^a	0.93011	0.91936	0.91288	0.90446	0.90067	0.89875	0.89534	0.89247
368.15 K, 97.13 kPa	0.92587	0.91861	0.90741	0.90120	0.89568	0.89498	0.89119	0.88854

[a] Results at these conditions not included in least-squares analysis. [b] Deviations of these points not shown in Figure 1 ($\Delta E > 8$ mV).

The solubility of CO_2 as a function of temperature and ionic strength and the dissociation constant for water were calculated from the expressions given by Peiper and Pitzer (*2*).

Equation 4 includes 22 adjustable parameters, each of which is in principle dependent on temperature. It is neither possible nor desirable to determine values of all these parameters from the results reported here. In particular, the $\beta^{(0)}_{K_2CO_3}$ and $\beta^{(0)}_{KHCO_3}$ parameters cannot be determined uniquely from these data. We have used these results to redetermine the temperature dependence of the $\beta^{(0)}_{K_2CO_3}$ and $\beta^{(1)}_{K_2CO_3}$ parameters. Interaction parameters for KCl(aq) at experimental temperatures were calculated from the equations given by Holmes and Mesmer (*15*). Parameters for KOH(aq) were assumed independent of temperature; the values reported by Pitzer and Mayorga (*16*) at 298.15 K were used. Values for $KHCO_3$(aq) parameters at 298.15 K are from Roy et al. (*1*). We assume these parameters have the same linear temperature dependence as those for sodium bicarbonate and adopt the temperature coefficients reported by Peiper and Pitzer (*2*). All mixing coefficients were assumed independent of temperature. We use the values reported by Roy et al. (*1*) in their full electrostatic mixing fit of the lower temperature results.

In our fitting of the data reported here, we adopt the values of $\beta^{(0)}_{K_2CO_3}$ and $\beta^{(1)}_{K_2CO_3}$ at 298.15 K and the linear temperature coefficients reported previously (*1*). Coefficients of quadratic terms in the temperature difference (T – 298.15) were determined for both $\beta^{(0)}$ and $\beta^{(1)}$ through least-squares analysis. The standard error of fit to these results was 0.9 mV. This error is significantly greater than the 0.5-mV fit deviation reported for this cell at lower temperatures and reflects the experimental difficulties encountered in this work. Fits of these results in which both the linear and quadratic temperature dependence parameters were optimized resulted in insignificant fit improvement. Similar deviations were noted for all runs, including those with $m_{CO_3} \neq m_{HCO_3}$, indicating that the assumption of temperature-independent mixing parameters did not materially affect fit quality. The K_2CO_3(aq) interaction parameters as a function of temperature are

$$\beta^{(0)}_{K_2CO_3} = 0.1288 + 1.1 \times 10^{-3}(T - 298.15) - (5.10 \pm 0.27) \times 10^{-6}(T - 298.15)^2$$

$$\beta^{(1)}_{K_2CO_3} = 1.433 + 4.36 \times 10^{-3}(T - 298.15) + (2.07 \pm 0.19) \times 10^{-5}(T - 298.15)^2$$

Stoichiometric and equilibrium molalities, equilibrium pressures of CO_2, water activities, osmotic coefficients, and solute activity coefficients calculated at 338.15–368.15 are listed in Table II

Table II. Calculated Excess Thermodynamic Properties of Mixed Potassium (Carbonate + Bicarbonate) Solutions[a]

	$m^{st}_{K_2X}$	m^{st}_{KY}	$m^{eq}_{X^{2-}}$	$m^{eq}_{Y^-}$	$m^{eq}_{Z^-}$	P_{CO_2}[b]	a_w	φ	γ_{K_2X}	γ_{KY}	γ_{KZ}
338.15 K	0.010	0.010	0.009	0.011	0.001	0.0002	0.99917	0.910	0.675	0.813	0.826
	0.050	0.050	0.049	0.051	0.001	0.0009	0.99614	0.856	0.502	0.687	0.723
	0.100	0.100	0.099	0.101	0.001	0.0019	0.99248	0.837	0.432	0.627	0.683
	0.200	0.200	0.199	0.200	0.001	0.0045	0.98529	0.822	0.369	0.568	0.655
	0.400	0.400	0.400	0.400	0.000	0.0114	0.97101	0.816	0.317	0.514	0.651
	0.600	0.600	0.600	0.600	0.000	0.0203	0.95651	0.823	0.294	0.487	0.673
	0.800	0.800	0.800	0.800	0.000	0.0314	0.94162	0.835	0.282	0.470	0.708
	1.000	1.000	1.000	1.000	0.000	0.0444	0.92630	0.850	0.277	0.459	0.752
	1.200	1.200	1.200	1.199	0.000	0.0591	0.91062	0.866	0.276	0.451	0.805
	1.400	1.400	1.400	1.399	0.000	0.0751	0.89467	0.883	0.278	0.444	0.865
	1.600	1.600	1.600	1.599	0.000	0.0921	0.87859	0.898	0.281	0.437	0.931
	1.800	1.800	1.800	1.799	0.000	0.1096	0.86250	0.912	0.286	0.430	1.005
348.15 K	0.010	0.010	0.009	0.011	0.001	0.0002	0.99916	0.910	0.670	0.811	0.823
	0.050	0.050	0.049	0.051	0.001	0.0011	0.99614	0.855	0.495	0.683	0.718
	0.100	0.100	0.099	0.101	0.001	0.0024	0.99248	0.836	0.426	0.624	0.679
	0.200	0.200	0.199	0.201	0.001	0.0057	0.98528	0.822	0.364	0.567	0.651
	0.400	0.400	0.400	0.400	0.001	0.0148	0.97091	0.819	0.313	0.516	0.650
	0.600	0.600	0.600	0.600	0.001	0.0271	0.95622	0.828	0.291	0.492	0.674
	0.800	0.800	0.800	0.800	0.000	0.0429	0.94103	0.843	0.281	0.479	0.711
	1.000	1.000	1.000	1.000	0.000	0.0624	0.92531	0.862	0.277	0.472	0.758
	1.200	1.200	1.200	1.199	0.000	0.0853	0.90912	0.881	0.277	0.467	0.812
	1.400	1.400	1.400	1.399	0.000	0.1113	0.89257	0.901	0.280	0.463	0.875
	1.600	1.600	1.600	1.599	0.000	0.1401	0.87578	0.920	0.285	0.460	0.944
	1.800	1.800	1.800	1.799	0.000	0.1711	0.85889	0.938	0.291	0.456	1.019
358.15 K	0.010	0.010	0.008	0.012	0.002	0.0003	0.99915	0.910	0.665	0.808	0.820
	0.050	0.050	0.048	0.052	0.002	0.0014	0.99614	0.853	0.489	0.679	0.714
	0.100	0.100	0.099	0.101	0.002	0.0030	0.99249	0.835	0.420	0.621	0.674
	0.200	0.200	0.199	0.200	0.001	0.0071	0.98528	0.822	0.358	0.565	0.647
	0.400	0.400	0.399	0.401	0.001	0.0188	0.97084	0.821	0.308	0.517	0.647
	0.600	0.600	0.600	0.600	0.001	0.0356	0.95599	0.832	0.287	0.497	0.673
	0.800	0.800	0.800	0.800	0.001	0.0581	0.94055	0.850	0.277	0.487	0.712
	1.000	1.000	1.000	1.000	0.001	0.0870	0.92447	0.872	0.274	0.483	0.761
	1.200	1.200	1.200	1.199	0.000	0.1226	0.90783	0.895	0.276	0.481	0.818
	1.400	1.400	1.400	1.399	0.000	0.1649	0.89073	0.918	0.280	0.481	0.882
	1.600	1.600	1.600	1.599	0.000	0.2139	0.87330	0.940	0.286	0.482	0.953
	1.800	1.800	1.800	1.799	0.000	0.2690	0.85570	0.961	0.293	0.482	1.029
368.15 K	0.010	0.010	0.008	0.012	0.002	0.0004	0.99914	0.911	0.660	0.806	0.817
	0.050	0.050	0.048	0.052	0.002	0.0017	0.99613	0.852	0.482	0.675	0.709
	0.100	0.100	0.098	0.102	0.002	0.0037	0.99249	0.833	0.413	0.617	0.669
	0.200	0.200	0.198	0.202	0.002	0.0087	0.98529	0.821	0.352	0.562	0.642
	0.400	0.400	0.399	0.401	0.001	0.0236	0.97080	0.822	0.302	0.518	0.644
	0.600	0.600	0.599	0.600	0.001	0.0461	0.95583	0.836	0.282	0.500	0.671
	0.800	0.800	0.800	0.800	0.001	0.0780	0.94017	0.856	0.273	0.494	0.712
	1.000	1.000	1.000	1.000	0.001	0.1207	0.92379	0.880	0.271	0.493	0.763
	1.200	1.200	1.200	1.199	0.001	0.1758	0.90675	0.906	0.272	0.495	0.821
	1.400	1.400	1.400	1.399	0.001	0.2445	0.88917	0.931	0.277	0.499	0.887
	1.600	1.600	1.600	1.599	0.000	0.3279	0.87117	0.957	0.284	0.503	0.958
	1.800	1.800	1.801	1.798	0.000	0.4263	0.85293	0.981	0.292	0.507	1.036

[a] $X = CO_3^{2-}$, $Y = HCO_3^-$, $Z = OH^-$. [b] Unit = 10^5 Pa.

for solutions of stoichiometrically equal carbonate and bicarbonate molalities.

Discussion

Values of excess thermodynamic properties calculated with the parameters reported here were compared with those calculated from previously reported parameters (*1*) over the temperature range $278.15 < T/K < 318.15$. The temperature dependence forms chosen ensure consistency of calculated values at 298.15. The largest differences noted were at the high concentration limit (1.8 mol·kg^{-1} K_2CO_3) at 278.15 and 318.15 K where the osmotic and activity coefficients differ by 0.004 and 0.003, respectively. Propagation of error through eq 3 indicates that these differences are within the fit uncertainty of the lower temperature study (<0.5 mV). It was therefore not necessary to refit the extensive lower temperature data set to obtain consistent excess thermodynamic properties for this system.

The form of eq 4 made it necessary to adopt in this work the temperature dependence of either the K_2CO_3(aq) or the $KHCO_3$(aq) ion interaction parameters determined at lower temperatures. We have chosen to fit parameters for K_2CO_3(aq); this choice is somewhat arbitrary. It should be noted that values of the pure electrolyte parameters for K_2CO_3(aq) determined in this manner are dependent on the values of $KHCO_3$(aq) pure electrolyte parameters. Experiments related more directly to pure electrolyte parameters of either K_2CO_3(aq) or $KHCO_3$(aq) are necessary to resolve this coupling.

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Excess Molar Enthalpies for the 1-Butanol–Benzene–Cyclohexane System at 25 °C

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Excess molar enthalpies at 25 °C were measured for 1-butanol–benzene–cyclohexane by use of an isothermal dilution calorimeter. The experimental results were well correlated with the UNIQUAC associated-solution model, which includes the dimerization constant and the constant for formation of higher polymers for the alcohol, and one solvation constant between the alcohol and benzene and binary interaction parameters.

Introduction

Studies on the thermodynamic properties of 1-butanol mixtures are in progress in this laboratory. This work reports excess molar enthalpies for 1-butanol–benzene–cyclohexane at 25 °C, measured by using an isothermal dilution calorimeter. Excess molar enthalpies for all the binary systems constituting the ternary system have been already published: 1-butanol–benzene (*1*); 1-butanol–cyclohexane (*2*); benzene–cyclohexane (*3*). The experimental values are compared with those calculated from the UNIQUAC associated-solution model (*4*).

Experimental Section

Analytical grade 1-butanol and cyclohexane of specified purity 99.8 mol %, purchased from Wako Pure Chemical Industries Ltd., were used directly. C.P. benzene was recrystallized three times. Gas chromatographic analysis did not detect any appreciable impurities in the reagents used. Densities of these compounds, measured with an Anton Paar DMA40 densimeter, were in close agreement with literature values (*4*).

The isothermal dilution calorimeter used for excess enthalpy measurements at 25 °C was the same as described previously (*3*). The uncertainty in the obtained excess enthalpies is ±0.5%. Three experimental runs were carried out for ternary mixtures formed by adding 1-butanol to a binary mixture of benzene and cyclohexane. A ternary mixture may be considered as a pseudobinary mixture composed of 1-butanol (component 1) and one binary mixture.

Value of H^E_{123} for one mole of the ternary mixture of composition x_1, x_2, and x_3 can be given as

$$H^E_{123} = \Delta H_m + (1 - x_1)H^E_{23} \tag{1}$$

where ΔH_m is the measured molar enthalpy for the pseudobinary mixture and H^E_{23} is the molar enthalpy for the initial binary benzene (2)–cyclohexane (3) mixture. Values of H^E_{23} at three specified compositions were interpolated by use of a spline-fit method.

Table I gives experimental excess molar enthalpies for 1-butanol (1)–benzene (2)–cyclohexane (3). The measured results were correlated by

$$H^E_{123} = H^E_{12} + H^E_{13} + H^E_{23} + x_1x_2x_3\Delta_{123} \tag{2}$$

where Δ_{123} is expressed by

$$\frac{\Delta_{123}}{RT} = \frac{\sum_{i=1}^{5} b_i(1 - 2x_1)^{i-1}}{1 - k(1 - 2x_1)} \tag{3}$$

Smoothing equations for the binary excess enthalpy data are shown in Table II. The smoothing equations for 1-butanol–benzene and benzene–cyclohexane were taken from the literature (*1*, *3*). We did not use the smoothing equation described by Veselý and Pick (*2*), because their equation was not suited for correlating the ternary experimental data. An unweighted least-squares method provided the values of coefficients of eq 3 and the standard deviation σ: $b_1 = 1.3915$, $b_2 = 0.7319$, $b_3 = -1.8773$, $b_4 = -1.3453$, $b_5 = 3.4113$, $k = 0.9182$, and $\sigma = 10.5$ J mol^{-1}. Figure 1 shows lines of constant ternary excess molar enthalpies calculated from eq 2 and 3.

Data Analysis by means of the UNIQUAC Associated-Solution Model

The UNIQUAC associated-solution model (*5*) assumes that only the alcohol dimerization constant ($A_1 + A_1 = A_2$) is different and the other constants ($A_i + A_1 = A_{i+1}$, $i > 1$) are equal and the alcohol forms complexes with benzene ($A_i + B = A_iB$). The model gives ternary excess molar enthalpy for 1-butanol (A)–benzene (B)–cyclohexane (C) by

$$H^E_{123} = \frac{h_A x_A K_2 \Phi_{A_1}{}^2}{\Phi_A(1 - K_A\Phi_{A_1})^2}[1 + K_{AB}r_A\Phi_{B_1}] + \frac{h_{AB}x_A K_{AB} r_A \Phi_{A_1}\Phi_{B_1}}{\Phi_A}\left[1 + \frac{K_2\Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] - \frac{h_A x_A K_2 \Phi^0{}_{A_1}{}^2}{(1 - K_A\Phi^0{}_{A_1})^2} - R\sum_I q_I x_I \frac{\sum_J \theta_J \dfrac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J \tau_{JI}} \tag{4}$$

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