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Thermodynamics of Electrolyte Solutions: Activity and Osmotic Coefficients of the Ternary System $KCl–BaCl_2–H_2O$ at 25, 35, and 45 °C

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The activity coefficients of KCl in the aqueous mixtures of $KCl–BaCl_2$ were determined by electromotive force measurements at 25, 35, and 45 °C and the total ionic strengths of 0.5, 1.0, 2.0, and 3.0 *m*. The Harned coefficients and Pitzer binary and ternary interaction parameters (${}^{E}\Theta$ and Ψ) were evaluated. Osmotic coefficients, excess free energies of mixing, and the activity coefficient of $BaCl_2$ were calculated at all the ionic strengths and temperatures studied.

Introduction

A wide variety of industrial geological and biochemical processes involve aqueous multicomponent electrolyte solutions. Christenson and Gieskes (*1*) determined the mean activity coefficients of aqueous KCl in $KCl–BaCl_2–H_2O$ at 25 °C and a total ionic strength of 1 *m* using a potassium-selective glass and Ag–AgCl electrodes. Robinson and Bower (*2*) measured the vapor pressures of this system isopiestically at 25 °C over an ionic strength range of 1.0–4.0 *m*. They have also calculated the activity coefficients of each salt and excess free energies of mixing in the mixture. Thus, the activity and osmotic coefficients of the system are not yet determined as a function of temperature. We are now reporting the activity coefficients of KCl and $BaCl_2$ in the mixture $KCl–BaCl_2–H_2O$ at 25, 35, and 45 °C over an ionic strength range of 0.5–3.0 *m*.

Experimental Section

The cell arrangement consisted of a potassium ion-selective electrode (Elico, India) and Ag–AgCl electrode immersed in a mixture of KCl and $BaCl_2$ aqueous solutions placed in a double-walled glass vessel whose temperature was maintained constant (±0.01 °C) by circulating thermostated water.

K ion-selective glass electrode	KCl (m_A) + $BaCl_2$ (m_B) + H_2O	AgCl, Ag electrode

The silver–silver chloride electrodes were prepared according to the thermal method (*3*). The electrodes were connected to a high-impedance ($\simeq 10^{12}$ Ω) unit gain amplifier. The output of this amplifier was measured by an electrometer (Keithley, Model DMM 191). The accuracy of the emf measurements was ±0.1 mV or better.

Analytical-grade potassium chloride (GR, S. Merk) and barium chloride (GR, Sarabhai) were used without further purification. The stock solutions were standardized volumetrically by a potentiometric titration against $AgNO_3$ solution with an accuracy of ±0.01%. All solutions were taken by weight. Also, all titrations and dilutions were made with weight burets.

At every ionic strength, the potassium ion-selective electrode was first calibrated with the aqueous KCl solutions of various molalities. Next, its selectivity toward Ba^{2+} ions was estimated by measuring the cell emf values with pure $BaCl_2$ solutions at several molalities. The third set consisted of the emf measurements in $KCl–BaCl_2–H_2O$ mixtures. For this set, the potentials were first measured by starting with pure KCl solution and adding aliquots of pure $BaCl_2$ solutions. Next, starting with pure $BaCl_2$ solution, aliquots of KCl solutions of the same ionic strength were successively added. The overlapping portion between these two experiments was used to test the reproducibility and accuracy of the measurements. All sets were repeated at least twice to get consistent and reproducible results.

Calculations and Discussion

The emf values of the potassium ion-selective electrode vs the Ag–AgCl electrode in the ternary system $KCl–BaCl_2–H_2O$ are given by the relation

$$E_{KCl\text{-}BaCl_2} = E_0 + k \log (a_K a_{Cl} + K' a_{Ba}{}^{1/2} a_{Cl}) \quad (1)$$

where K' is the selectivity coefficient of potassium ion-selective electrode for Ba^{2+} ions and $k = 2.303RT/nF$, which is the Nernst slope. In pure KCl solutions, $a_{Ba} = 0$, and, therefore, eq 1 reduces to

$$E_{KCl} = E_0 + k \log (a_K a_{Cl}) \quad (2)$$

Similarly in pure $BaCl_2$ solutions, $a_K = 0$, and, therefore, eq 1 could be rearranged as

$$K' = (1/a_{BaCl_2}{}^{3/2}) 10^{(E_{BaCl2} - E_0)/k} \quad (3)$$

At each ionic strength, the emf data obtained in the calibration run was fitted to eq 2 by a least-squares procedure to find the E_0 and k values. The activity coefficients for pure aqueous KCl were calculated with the ion interaction parameters (β^0, β^1, and

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Table I. Mean Activity Coefficients of KCl in $KCl-BaCl_2-H_2O$ Mixtures

$I = 0.5$		$I = 1.0$		$I = 2.0$		$I = 3.0$	
y_B	$-\log \gamma_\pm$	y_B	$-\log \gamma_\pm$	y_B	$-\log \gamma_\pm$	y_B	$-\log \gamma_\pm$
T = 25 °C							
0.0000	0.1872	0.0000	0.2184	0.0000	0.2408	0.0000	0.2438
0.1104	0.1865	0.1033	0.2175	0.1110	0.2403	0.1124	0.2451
0.1988	0.1860	0.1872	0.2167	0.1999	0.2398	0.2021	0.2457
0.2712	0.1856	0.2568	0.2161	0.2726	0.2392	0.2753	0.2459
0.3317	0.1853	0.3154	0.2156	0.3332	0.2387	0.3362	0.2458
0.3828	0.1850	0.3654	0.2152	0.3845	0.2383	0.3877	0.2457
0.4267	0.1849	0.4086	0.2149	0.4284	0.2378	0.4318	0.2455
0.4478	0.1848	0.4463	0.2146	0.4595	0.2375	0.4439	0.2454
0.4648	0.1847	0.4738	0.2144	0.4665	0.2374	0.4699	0.2452
0.4740	0.1847	0.4795	0.2143	0.4858	0.2372	0.4701	0.2452
0.4981	0.1846	0.5002	0.2142	0.4998	0.2371	0.4995	0.2449
0.5034	0.1846	0.5090	0.2141	0.5152	0.2369	0.5033	0.2449
0.5275	0.1845	0.5296	0.2139	0.5293	0.2367	0.5327	0.2446
0.5367	0.1845	0.5352	0.2139	0.5484	0.2365	0.5328	0.2446
0.5537	0.1844	0.5627	0.2137	0.5554	0.2364	0.5588	0.2443
0.5747	0.1844	0.6002	0.2135	0.5862	0.2361	0.5709	0.2441
0.6186	0.1842	0.6430	0.2132	0.6297	0.2355	0.6149	0.2435
0.6697	0.1841	0.6924	0.2128	0.6800	0.2348	0.6662	0.2427
0.7299	0.1840	0.7501	0.2124	0.7392	0.2340	0.7268	0.2416
0.8022	0.1839	0.8183	0.2120	0.8095	0.2329	0.7997	0.2400
0.8902	0.1838	0.9001	0.2115	0.8948	0.2315	0.8887	0.2377
T = 35 °C							
0.0000	0.1875	0.0000	0.2171	0.0000	0.2370	0.0000	0.2380
0.1047	0.1869	0.1079	0.2163	0.1195	0.2366	0.1003	0.2391
0.1895	0.1865	0.1948	0.2157	0.2135	0.2362	0.1823	0.2398
0.2597	0.1863	0.2662	0.2152	0.2894	0.2358	0.2506	0.2401
0.3186	0.1860	0.3260	0.2148	0.3519	0.2354	0.3084	0.2403
0.3689	0.1859	0.3768	0.2145	0.4043	0.2351	0.3579	0.2403
0.4123	0.1858	0.4205	0.2143	0.4488	0.2348	0.4008	0.2402
0.4501	0.1857	0.4584	0.2141	0.4488	0.2348	0.4383	0.2401
0.4656	0.1856	0.4644	0.2141	0.4750	0.2346	0.4590	0.2400
0.4833	0.1856	0.4907	0.2139	0.4872	0.2345	0.4714	0.2400
0.4919	0.1856	0.4917	0.2139	0.5044	0.2343	0.4853	0.2399
0.5127	0.1855	0.5201	0.2138	0.5206	0.2342	0.5008	0.2398
0.5214	0.1855	0.5212	0.2138	0.5377	0.2341	0.5147	0.2397
0.5390	0.1855	0.5474	0.2136	0.5499	0.2340	0.5271	0.2396
0.5545	0.1855	0.5533	0.2136	0.5757	0.2337	0.5480	0.2394
0.5922	0.1854	0.5911	0.2134	0.5758	0.2337	0.5858	0.2391
0.6354	0.1854	0.6343	0.2132	0.6195	0.2333	0.6292	0.2387
0.6854	0.1853	0.6843	0.2130	0.6706	0.2328	0.6796	0.2380
0.7439	0.1853	0.7430	0.2127	0.7307	0.2322	0.7388	0.2372
0.8133	0.1853	0.8126	0.2125	0.8028	0.2314	0.8093	0.2360
0.8971	0.1854	0.8966	0.2122	0.8906	0.2304	0.8946	0.2343
T = 45 °C							
0.0000	0.1887	0.0000	0.2175	0.0000	0.2355	0.0000	0.2350
0.1095	0.1882	0.1004	0.2169	0.0956	0.2353	0.1284	0.2362
0.1974	0.1879	0.1826	0.2164	0.1745	0.2350	0.2276	0.2368
0.2696	0.1877	0.2509	0.2160	0.2407	0.2348	0.3065	0.2371
0.3298	0.1875	0.3087	0.2157	0.2971	0.2345	0.3708	0.2371
0.3508	0.1874	0.3583	0.2155	0.3457	0.2343	0.4242	0.2371
0.4247	0.1873	0.4012	0.2153	0.3880	0.2341	0.4502	0.2370
0.4466	0.1873	0.4387	0.2152	0.4252	0.2339	0.4692	0.2370
0.4627	0.1873	0.4499	0.2151	0.4460	0.2338	0.4764	0.2369
0.4727	0.1873	0.4718	0.2151	0.4581	0.2337	0.5059	0.2368
0.4960	0.1873	0.4761	0.2150	0.4721	0.2337	0.5077	0.2368
0.5022	0.1873	0.5012	0.2149	0.4875	0.2336	0.5392	0.2366
0.5254	0.1872	0.5055	0.2149	0.5015	0.2335	0.5410	0.2366
0.5355	0.1872	0.5275	0.2149	0.5138	0.2334	0.5701	0.2364
0.5516	0.1872	0.5388	0.2148	0.5349	0.2333	0.5772	0.2364
0.5735	0.1872	0.5768	0.2147	0.5729	0.2330	0.5957	0.2363
0.6174	0.1872	0.6206	0.2146	0.6168	0.2328	0.6209	0.2361
0.6686	0.1872	0.6715	0.2144	0.6680	0.2324	0.6719	0.2356
0.7290	0.1873	0.7316	0.2143	0.7285	0.2319	0.7319	0.2350
0.8014	0.1874	0.8035	0.2142	0.8010	0.2314	0.8037	0.2340
0.8897	0.1875	0.8910	0.2140	0.8895	0.2306	0.8912	0.2327

C^ϕ) values of Holmes and Mesmer (*4*) and for pure $BaCl_2$ solutions from the works of Kim and Frederick (*5*) and Silvester and Pitzer (*6*). The emf data obtained in the second set along with the E_0 and k values obtained from the calibration run were substituted in eq 3 to find the selectivity coefficient (K') values. The selectivity coefficient values at all ionic strengths and temperatures studied were $\leq 1 \times 10^{-4}$. Therefore, the $K' a_{Ba}^{1/2} a_{Cl}$ term in eq 1 was neglected. Then, the cell emf values for aqueous $KCl-BaCl_2$ mixtures could be described by eq 2 itself. This eq 2 could be rearranged as

$$\gamma_\pm^2 = (1/m_K m_{Cl}) 10^{(E_{KCl-BaCl_2} - E_0)/k} \quad (4)$$

Table II. Harned Coefficients (α_{AB} and β_{AB}), Pitzer Binary and Ternary Interaction Parameters (${}^s\Theta$ and Ψ), and Friedman Parameters (g_0 and g_1) in the System KCl–$BaCl_2$–H_2O

I	$10^3\alpha_{AB}$	$10^3\beta_{AB}$	10^5RMSD for α_{AB} and β_{AB}	$10^2\,{}^s\Theta$	$10^2\Psi$	10^5RMSD for ${}^s\Theta$ and Ψ	10^3g_0	10^3g_1
				T = 25 °C				
0.5	-6.804	3.262	3.33	3.440	-2.903	2.57	-6.827	4.203
1.0	-9.284	1.735	2.23	3.376	-2.657	2.73	1.720	2.523
2.0	-3.707	-7.504	2.90	3.437	-2.728	2.67	8.919	1.794
3.0	14.10	-23.66	2.92	3.431	-2.712	2.37	14.32	1.868
common values				3.404	-2.700	2.77		
				T = 35 °C				
0.5	-5.919	-4.044	3.61	3.568	-2.278	2.93	-9.832	4.434
1.0	-7.744	2.539	2.69	3.571	-2.311	2.69	-0.875	2.686
2.0	-2.569	-5.416	3.27	3.644	-2.399	2.90	6.258	1.781
3.0	13.27	-19.40	3.22	3.591	-2.361	2.64	11.28	1.625
common values				3.605	-2.369	2.89		
				T = 45 °C				
0.5	-4.926	4.062	3.73	3.816	-2.012	2.73	-12.30	4.664
1.0	-6.588	2.971	3.60	3.772	-1.950	3.18	-3.083	2.849
2.0	-2.024	-3.954	3.19	3.837	-2.055	2.87	3.896	1.814
3.0	11.55	-15.81	3.19	3.790	-2.019	2.86	8.575	1.505
common values				3.812	-2.031	3.03		

Table III. Osmotic Coefficients (Φ_m), Excess Free Energies of Mixing ($\Delta_m G^E$, J kg^{-1} of Water), and Mean Activity Coefficients (γ) of $BaCl_2$ in KCl–$BaCl_2$–H_2O System

	I = 0.5			I = 1.0			I = 2.0			I = 3.0		
y_B	Φ_m	$-\log \gamma_{BaCl_2}$	$\Delta_m G^E$	Φ_m	$-\log \gamma_{BaCl_2}$	$\Delta_m G^E$	Φ_m	$-\log \gamma_{BaCl_2}$	$\Delta_m G^E$	Φ_m	$-\log \gamma_{BaCl_2}$	$\Delta_m G^E$
						T = 25 °C						
0.0	0.9007	0.3633	0	0.8990	0.4140	0	0.9136	0.4478	0	0.9374	0.4566	0
0.1	0.8972	0.3606	-0.1908	0.8960	0.4108	0.8406	0.9104	0.4437	9.27	0.9318	0.4516	31.73
0.2	0.8932	0.3581	-0.4252	0.8927	0.4077	1.2854	0.9075	0.4397	15.87	0.9275	0.4464	55.12
0.3	0.8888	0.3558	-0.6715	0.8891	0.4047	1.4159	0.9049	0.4357	20.05	0.9245	0.4412	70.61
0.4	0.8838	0.3536	-0.8943	0.8850	0.4020	1.3125	0.9025	0.4319	22.03	0.9229	0.4359	78.68
0.5	0.8781	0.3516	-1.0623	0.8805	0.3994	1.0532	0.9004	0.4281	22.05	0.9226	0.4305	79.84
0.6	0.8715	0.3497	-1.1442	0.8752	0.3970	0.7130	0.8983	0.4245	20.32	0.9237	0.4251	74.61
0.7	0.8638	0.3480	-1.1087	0.8690	0.3947	0.3660	0.8962	0.4209	17.05	0.9262	0.4196	63.52
0.8	0.8548	0.3465	-0.9260	0.8617	0.3926	0.0850	0.8940	0.4174	12.45	0.9300	0.4141	47.08
0.9	0.8441	0.3452	-0.5660	0.8529	0.3907	-0.0602	0.8914	0.4141	6.71	0.9353	0.4085	25.76
1.0	0.8311	0.3440	0	0.8422	0.3890	0	0.8881	0.4108	0	0.9419	0.4028	0
						T = 35 °C						
0.0	0.9021	0.3672	0	0.9022	0.4169	0	0.9196	0.4479	0	0.9453	0.4531	0
0.1	0.8983	0.3646	-0.3597	0.8989	0.4139	0.2999	0.9163	0.4442	7.110	0.9401	0.4487	26.09
0.2	0.8941	0.3623	-0.7339	0.8954	0.4110	0.3044	0.9133	0.4407	12.02	0.9359	0.4443	45.22
0.3	0.8894	0.3600	-1.086	0.8915	0.4083	0.1024	0.9104	0.4373	14.98	0.9329	0.4399	57.78
0.4	0.8841	0.3580	-1.379	0.8870	0.4058	-0.2182	0.9077	0.4340	16.23	0.9310	0.4355	64.23
0.5	0.8781	0.3561	-1.579	0.8820	0.4035	-0.5726	0.9049	0.4308	15.98	0.9301	0.4311	65.00
0.6	0.8712	0.3544	-1.652	0.8762	0.4014	-0.8778	0.9021	0.4278	14.47	0.9304	0.4267	60.58
0.7	0.8631	0.3529	-1.563	0.8695	0.3995	-1.052	0.8992	0.4249	11.92	0.9316	0.4222	51.43
0.8	0.8536	0.3516	-1.279	0.8615	0.3977	-1.016	0.8958	0.4221	8.519	0.9338	0.4178	38.00
0.9	0.8424	0.3504	-0.7687	0.8519	0.3962	-0.6912	0.8918	0.4194	4.483	0.9369	0.4134	20.72
1.0	0.8288	0.3494	0	0.8402	0.3948	0	0.8867	0.4169	0	0.9409	0.4089	0
						T = 45 °C						
0.0	0.9026	0.3273	0	0.9041	0.4215	0	0.9237	0.4501	0	0.9507	0.4521	20.95
0.1	0.8986	0.3698	-0.5070	0.9007	0.4186	-0.1854	0.9204	0.4468	5.113	0.9460	0.4483	20.95
0.2	0.8942	0.3675	-1.004	0.8969	0.4159	-0.5790	0.9173	0.4437	8.446	0.9422	0.4446	36.11
0.3	0.8893	0.3654	-1.450	0.8927	0.4135	-1.084	0.9143	0.4407	10.25	0.9393	0.4409	45.89
0.4	0.8838	0.3634	-1.808	0.8880	0.4112	-1.606	0.9112	0.4379	10.78	0.9372	0.4373	50.71
0.5	0.8774	0.3617	-2.038	0.8826	0.4091	-2.050	0.9081	0.4353	10.26	0.9360	0.4337	51.01
0.6	0.8702	0.3601	-2.104	0.8764	0.4072	-2.328	0.9047	0.4327	8.937	0.9355	0.4302	47.24
0.7	0.8618	0.3587	-1.968	0.8691	0.4055	-2.349	0.9009	0.4304	7.029	0.9356	0.4267	39.83
0.8	0.8519	0.3575	-1.596	0.8606	0.4041	-2.026	0.8966	0.4282	4.762	0.9364	0.4233	29.22
0.9	0.8401	0.3565	-0.9513	0.8502	0.4028	-1.271	0.8913	0.4262	2.349	0.9377	0.4199	15.81
1.0	0.8259	0.3556	0	0.8377	0.4017	0	0.8847	0.4243	0	0.9392	0.4165	0

Thus, the activity coefficients of KCl in aqueous KCl–$BaCl_2$ mixtures were calculated by substituting the cell emf ($E_{KCl-BaCl_2}$) in eq 4. These experimental mean activity coefficients ($\gamma_\pm$) of KCl in aqueous KCl–$BaCl_2$ mixtures at the total ionic strengths of 0.5, 1.0, 2.0, and 3.0 m are given in Table I at different values of ionic strength fraction (y_B) of $BaCl_2$ where $y_B = 3m_{BaCl_2}/(m_{KCl} + 3m_{BaCl_2})$. The log $\gamma_\pm$ values at 25 °C are plotted as a function of y_B in Figure 1. From Figure 1, it is evident that our log $\gamma_\pm$ values are in good agreement with the activity coefficient data of Christenson and Gieskes (*1*). These activity coefficient values were fitted to the Harned (*7*) equation given below:

$$\log \gamma_A = \log \gamma_A{}^\circ - \alpha_{AB}y_B - \beta_{AB}y_B{}^2 \qquad (5)$$

where log $\gamma_A{}^\circ$ is the activity coefficient of pure KCl at the same ionic strength as that of the mixture. These Harned coefficient

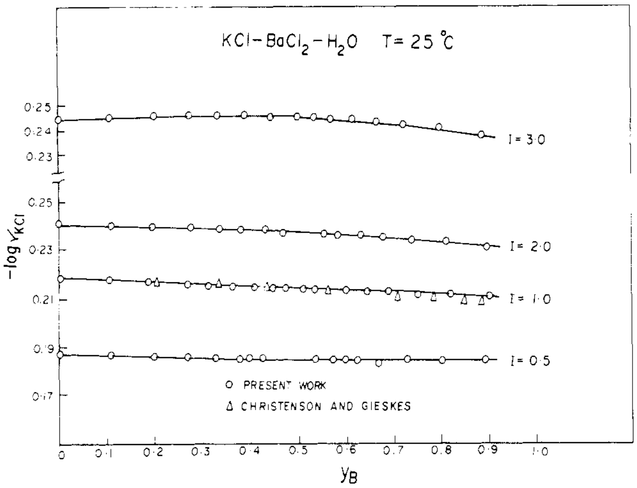

Figure 1. Plot of $-\log \gamma_{KCl}$ against y_{BaCl_2} at different ionic strengths.

(α_{AB} and β_{AB}) values are listed in Table II.

The activity coefficients of KCl in constant ionic strength mixtures of KCl–BaCl$_2$–H$_2$O are described by the Pitzer equation, which is given in the literature (*8–10*). The experimental activity coefficient data was fitted to this equation to calculate the binary interaction coefficients ($^s\Theta_{KBa}$) and ternary interaction coefficients (Ψ_{KBaCl}) at every ionic strength. These $^s\Theta$ and Ψ values are also listed in Table II along with the corresponding root mean square deviation (RMSD) values. Next, the common $^s\Theta$ and Ψ values were calculated at each of the ionic strengths and temperatures studied with use of a linear least-squares program. From Table II, it is evident that these common $^s\Theta$ and Ψ values are nearly constant at each temperature and are independent of ionic strength as expected according to the Pitzer formalism (*8*). These $^s\Theta = 0.034$ and $\Psi = -0.027$ values obtained in the present work at 25 °C are in reasonable agreement with the values ($^s\Theta = 0.01$ and $\Psi = -0.017$) reported by Pitzer (*11*) using the isopiestic data of Robinson and Bower (*2*). The $^s\Theta$ and Ψ values (cf. Table II) at 25, 35, and 45 °C give the temperature derivatives of $^s\Theta$ and Ψ as $\partial\,^s\Theta/\partial T = (2.0 \pm 0.2) \times 10^{-4}$ and $\partial \Psi/\partial T = (3.3 \pm 0.2) \times 10^{-4}$. These values are in the same range as reported by Pitzer (*12*) for the similar systems. Next, with these common $^s\Theta$ and Ψ values, the osmotic coefficients of the mixtures were calculated at each of the ionic strengths and temperatures studied with use of the Pitzer equation (*13*). These osmotic coefficients are listed in Table III. These osmotic coefficients are in agreement with the experimental data of Robinson and Bower (*2*) with an RMSD of 9.1×10^{-3}. Also, the activity coefficients of the second component, i.e., BaCl$_2$, were calculated at each of the ionic strengths and temperatures studied with the respective $^s\Theta$ and Ψ values in the appropriate Pitzer equation (*8*, *9*). These values are also listed in Table III.

The excess Gibbs free energies of mixing for KCl–BaCl$_2$–H$_2$O system were calculated with the equation

$$\Delta_m G^E = Y_A[\ln (\gamma_A/\gamma_A{}^\circ) + (\Phi_A - \Phi_m)] + Y_B[\ln (\gamma_B/\gamma_B{}^\circ) + (\Phi_B - \Phi_m)] \quad (6)$$

where $Y_A = \nu_A y_A m_A RT$; $Y_B = \nu_B y_B m_B RT$, and the other symbols have their usual significance (*9*). These values are also listed in Table III. These excess Gibbs free energies were fitted to the Friedman equation (*14*)

$$\Delta_m G^E = I^2 RTy(1 - y)[g_0 + (1 - 2y)g_1] \quad (7)$$

The Friedman parameters g_0 and g_1 were evaluated by a least-squares regression procedure, and the values are listed in Table II. As the ionic strength and also temperature are increasing, the $\Delta_m G^E$ values are changing in both magnitude and sign.

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Registry No. KCl, 7447-40-7; BaCl$_2$, 10361-37-2.

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Isobaric Vapor–Liquid Equilibria in the Systems Propyl Bromide–Methyl Ethyl Ketone, Methyl Ethyl Ketone–*p*-Xylene, and Vinyl Acetate–Methyl Methacrylate

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Vapor–liquid equilibria for the title systems have been determined at 760 mmHg. The two methyl ethyl ketone systems exhibit positive deviations from ideal behavior, no azeotropes are present, and the third system behaves ideally. An empirical equation was used to correlate the boiling points with the composition of the liquid phase.

The present work is part of our program for determining vapor–liquid equilibrium (VLE) data for organic systems in which one of the components is a bromide. The only literature reference is that of Chandrashekara and Seshadri (*1*) who measured the vapor–liquid equilibria of methyl ethyl ketone (MEK) and *p*-xylene at 685 mmHg. We claim that their data are not acceptable because they show that the activity coefficients of

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