Table IV. Average Deviations between the Predicted and Experimental Values by the Bubble Point Prediction

pressure, mmHg	$\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ at each pressure		$\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ of 1 atm pressure		Λ_{12}, Λ_{21} of 1 atm pressure	
	$\Delta y_1{}^a$	Δt^b	$\Delta y_1{}^a$	Δt^b	$\Delta y_1{}^a$	Δt^b
760.0	0.003	0.2	0.003	0.2	0.003	0.2
400.0	0.004	0.1	0.005	0.3	0.006	0.4
200.0	0.005	0.1	0.006	0.3	0.008	0.5
100.0	0.006	0.1	0.004	0.4	0.007	0.6
50.0	0.005	0.2	0.005	0.4	0.010	0.7

[a] $\Delta y_1 = \Sigma|y_{1,\mathrm{calcd}} - y_{1,\mathrm{exptl}}|/n$. [b] $\Delta t = \Sigma|t_{\mathrm{calcd}} - t_{\mathrm{exptl}}|/n$. n = number of data.

Glossary

g^E	molar excess Gibbs energy, cal/mol
P	total pressure, mmHg
p_i	vapor pressure of pure substance i, mmHg
Q	Q function ($=g^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$)
R	gas constant, cal/(mol K)
T, t	temperature, K, °C
v_i	molar liquid volume of pure i at temperature T, cm/mol
x_i, y_i	mole fraction composition of component i in the liquid and vapor phases

Greek Letters

γ_i	i component activity coefficient of liquid phase
Λ_{12}, Λ_{21}	Wilson parameters defined by eq 2
$\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$	Wilson parameters, cal/mol

Literature Cited

(1) Hala, E., Wichterle, I., Polak, J., Boublik, T., "Vapor Liquid Equilibrium Data at Normal Pressures", Pergamon Press, Oxford, 1968, p 379.
(2) Herington, E. F. G., *J. Inst. Pet., London*, **37**, 457 (1951).
(3) Markuzin, N. P., Pavlova, L. M., *Zh. Prikl. Khim.* (*Leningrad*), **44**, 311 (1971).
(4) Michishita, T., Arai, Y., Saito, S., *Kagaku Kogaku*, **35**, 111 (1971).
(5) Rose, A., Williams, E. T., *Ind. Eng. Chem.*, **47**, 1528 (1955).
(6) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds", Elsevier, Amsterdam, 1950, pp 60 and 150.
(7) Vilcu, R., Cenuse, Z., *Rev. Roum. Chim.*, **17**, 367 (1972).
(8) Wilson, G. M., *J. Am. Chem. Soc.*, **86**, 127 (1964).
(9) Yerazunis, S., Plowright, J. D., Smola, F. M., *AIChE J.*, **10**, 660 (1964).

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Thermodynamic Properties of the Molten Salt System Cesium Bromide–Cuprous Bromide

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Molar volumes, excess molar volumes, partial molar volumes, and molar volume expansion coefficients were calculated for the binary molten salt system cesium bromide–cuprous bromide.

The experimental procedures and density results obtained in the system cesium bromide–cuprous bromide have been described previously (**6**). The temperature coefficients of the densities were evaluated at nine mole fractions over the complete composition range and in the temperature range 507–950 °C, using the method of Archimedean displacement.

This paper reports on the calculation of molar volumes, excess molar volumes, partial molar volumes, and molar volume expansion coefficients in the system cesium bromide–cuprous bromide.

Density and Temperature Coefficients of the Density

The experimental density data (*6*) were fitted to equations of the form

$$\rho = a - bT \qquad (1)$$

where ρ is in grams per cubic centimeter and T in Kelvin, and are listed in Table I. Figure 1 gives an overview of the densities, calculated from the data in Table I, over the entire composition range at three chosen temperatures.

Table I. Least-Squares Fits for the Densities Fitted to Equation 1

mole % of CsBr	a, g cm^{-3}	10^3b, g cm^{-3} K^{-1}	std dev	temp range, K
100.000	4.244_9	1.223	a	a
85.097	4.283_4	1.323	0.0019	918–1226
74.239	4.451_0	1.326	0.0020	880–1223
58.763	4.586_4	1.377	0.0028	870–1222
40.543	4.617_3	1.231	0.0021	850–1226
30.000	4.932_2	1.400	0.0027	861–1223
19.961	5.021_7	1.300	0.0035	849–1227
10.467	5.085_8	1.141	0.0058	840–1224
0.000[b]	5.282_8	0.916	0.0067	780–1224

[a] See ref 4. [b] Pure CuBr.

Molar Volumes and Excess Molar Volumes

Calculated values for molar volumes, standard deviations in molar volumes, ideal molar volumes, and excess molar volumes at three chosen temperatures are listed in Table II. Molar volumes V_M, ideal molar volumes V_I, and excess molar volumes V_E were calculated from the equations

$$V_M = (1/\rho)\sum x_iM_i \qquad (2)$$

$$V_I = \sum(x_iM_i/\rho_i) \qquad (3)$$

$$V_E = (1/\rho)\sum x_iM_i - \sum(x_iM_i/\rho_i) \qquad (4)$$

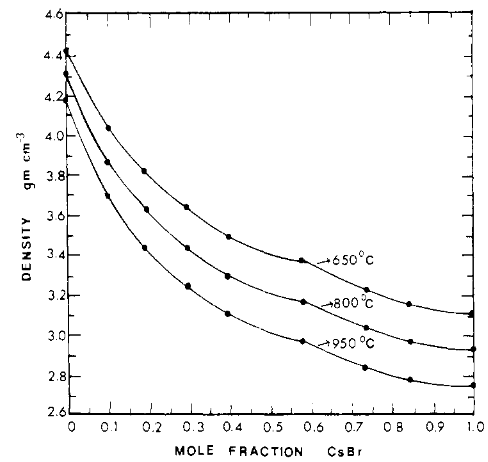

Figure 1. Densities of the CsBr–CuBr system as calculated at 650, 800 and 950 °C, from the data in Table I.

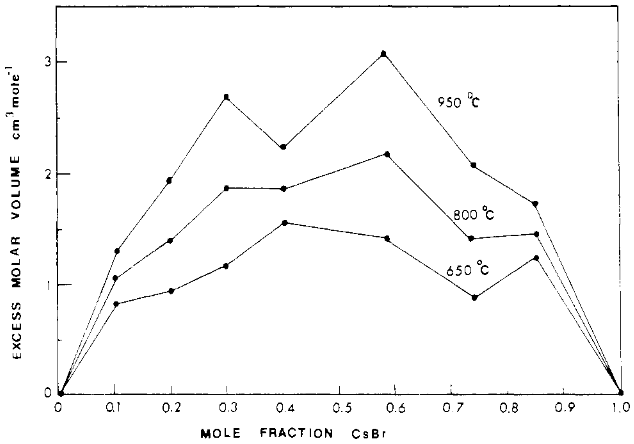

Figure 2. Excess molar volumes of the CsBr–CuBr system as calculated at 650, 800, and 950 °C.

where ρ = density of the mixture and ρ_i, x_i, and M_i are the density, mole fraction, and molecular mass of the ith component, respectively.

The standard deviations in molar volumes were calculated by using the standard deviations in densities (Table I).

Figure 2 shows the excess molar volumes over the entire composition range at three chosen temperatures.

The molar volumes of the melt mixtures as a function of composition over the entire range at the three chosen temperatures can be found in Figures 3–5.

Partial Molar Volumes

Partial molar volumes were determined by using the method of intercepts (*7*)

$$V_M = x_B \, dV_M/dx_B + \bar{V}_A \qquad (5)$$

where

x_B = mole fraction of component B

$\bar{V}_A$ = partial molar volume of component A

From the latter equation it can be seen that if V_M is plotted vs. x_B and a tangent drawn to the curve at any point on the curve, corresponding to a definite mole fraction x_B', the intercept at $x_B = 0$ is $\bar{V}_A$. It can readily be shown that the intercept on the other axis, where $x_B = 1$ or $x_A = 0$, is the partial molar volume of B, $\bar{V}_B$.

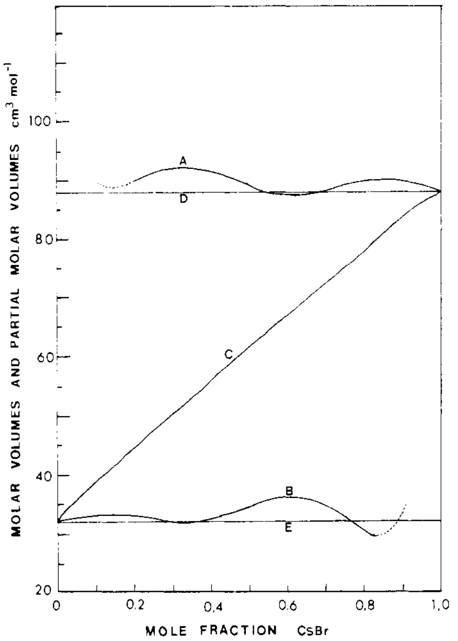

Figure 3. Molar volumes of mixture and partial molar volumes of CsBr and CuBr as a function of composition at 650 °C: A, partial molar volume CsBr; B, partial molar volume CuBr; C, molar volumes; D, molar volume CsBr; E, molar volume CuBr.

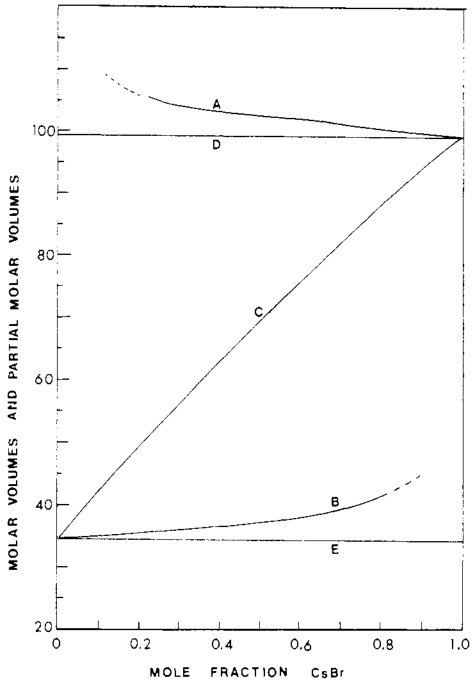

Figure 4. Molar volumes of mixture and partial molar volumes of CsBr and CuBr as a function of composition at 800 °C: A, partial molar volume CsBr; B, partial molar volume CuBr; C, molar volumes; D, molar volume CsBr; E, molar volume CuBr.

Figures 3–5 give the molar volume of the mixture and the partial molar volumes of CsBr and CuBr, as functions of composition, at 650, 800, and 950 °C, respectively.

Molar Volume Expansion Coefficients

At constant pressure and composition the molar volume of a solution is a function of temperature only.

The slope of a curve with axes molar volume and temperature $(\delta V_M/\delta T)_{Px_A}$, gives the rate of change of molar volume with temperature at a fixed composition.

Table II. Properties of the CsBr System as Calculated at 923, 1073, and 1223 K Using Data from Table I

mole % CsBr	mole % CsBr	molecular mass, g $\Sigma x_i m_i$	density (ρ), g cm^{-3}			molar volumes (V_m), cm^3 mol^{-1}			std dev V_m, cm^3 mol^{-1}			ideal molar volumes, cm^3 mol^{-1}			excess molar volumes, cm^3 mol^{-1}		
			923 K	1073 K	1223 K	923 K	1073 K	1223 K	923 K	1973 K	1223 K	923 K	1073 K	1223 K	923 K	1073 K	1223 K
100.000	0.000	272.81	3.115_7	2.932_2	2.748_7	87.56_0	93.03_9	99.25_1				87.56_0	93.03_9	99.25_1	0	0	0
85.097	14.903	253.53	3.146_3	2.961_5	2.776_7	80.58_0	85.60_8	91.30_6	0.09_7	0.10_9	0.12_5	79.32_7	84.14_6	89.59_5	1.25	1.46	1.71
74.239	25.761	239.49	3.227_1	3.028_2	2.829_3	74.21_2	79.08_6	84.64_6	0.09_2	0.10_5	0.11_9	73.33_2	77.66_6	82.56_1	0.88	1.42	2.09
58.763	41.237	219.47	3.315_4	3.108_9	2.902_3	66.19_7	70.59_4	75.61_9	0.11_2	0.12_7	0.14_6	64.78_4	68.43_0	72.53_4	1.41	2.16	3.09
40.543	59.457	195.90	3.481_1	2.296_4	3.111_8	56.27_5	59.43_0	62.95_4	0.06_8	0.07_6	0.08_5	54.72_1	57.55_7	60.73_0	1.56	1.87	2.22
30.000	70.000	182.26	3.640_0	3.430_0	3.220_0	50.07_1	53.13_7	56.60_3	0.07_4	0.08_4	0.09_4	48.89_8	51.26_5	53.89_9	1.17	1.87	2.70
19.961	80.039	169.27	3.821_8	3.626_8	3.341_6	44.29_1	46.67_2	49.32_4	0.08_1	0.09_0	0.10_1	43.35_3	45.27_4	47.39_5	0.94	1.40	1.93
10.467	89.533	156.99	4.032_7	3.861_5	3.690_4	38.92_9	40.65_5	42.54_0	0.11_6	0.12_2	0.13_4	38.11_0	39.60_8	41.24_1	0.82	1.05	1.30
0.000	100.000	143.45	4.437_3	4.299_9	4.162_5	32.32_8	33.36_1	34.46_3	0.09_8	0.10_4	0.11_1	32.32_8	33.36_1	34.46_3	0	0	0

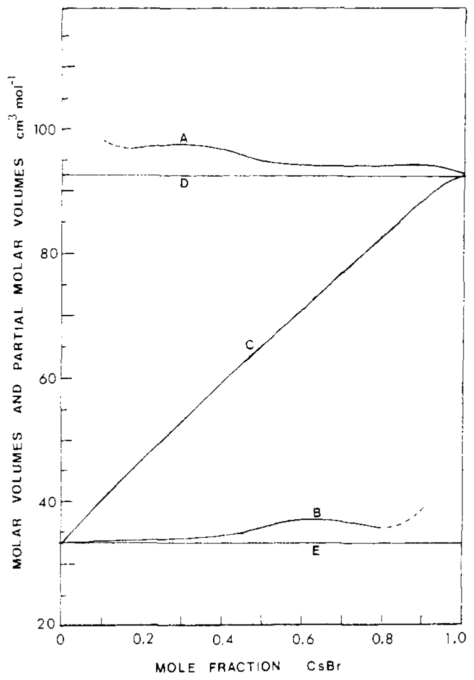

Figure 5. Molar volumes of mixture and partial molar volumes of CsBr and CuBr as a function of composition at 950 °C: A, partial molar volume CsBr; B, partial molar volume CuBr; C, molar volumes; D, molar volume CsBr; E, molar volume CuBr.

Table III. Molar Expansion Coefficients, α, of the CsBr-CuBr System

mole fraction CsBr	molar volume expansion coefficients (α) $10^4\alpha$, K^{-1}		
	923 K	1073 K	1223 K
1.0000	3.927	4.172	4.451
0.8510	3.916	4.160	4.437
0.7424	4.109	4.379	4.687
0.5876	4.153	4.429	4.745
0.4054	3.536	3.734	3.956
0.3000	3.846	4.082	4.348
0.1996	3.402	3.584	3.788
0.1047	2.829	2.955	3.092
0.0000	2.064	2.130	2.201

The molar volume expansion coefficient (*2*, *3*, *8*) or the expansivity, α, is defined as

$$\alpha = \frac{1}{V_M}\left(\frac{\delta V_M}{\delta T}\right)_{Px_A} \tag{6}$$

and can be calculated as follows:

$$\alpha = \frac{1}{V_M}\frac{b\sum x_iM_i}{(a - bT)^2} \tag{7}$$

because

$$V_M = \frac{\text{molecular mass}}{\text{density}} = \frac{\sum x_iM_i}{a - bT} \tag{8}$$

and

$$\frac{\delta V_M}{\delta T} = \frac{b\sum x_iM_i}{(a - bT)^2} \tag{9}$$

Table III and Figure 6 give the expansivities over the whole composition range at the three chosen temperatures.

Discussion. Mathematical Determination of Partial Molar Volumes

Functions from polynomial, quadratic, and cubic splines were fitted by the standard method of least squares to obtain the

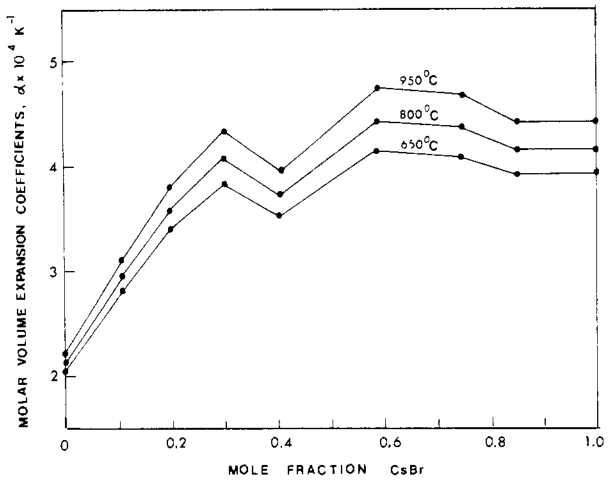

Figure 6. Molar volume expansion coefficients (α) of the CsBr-CuBr system at 650, 800, and 950 °C as a function of composition.

relevant partial molar volumes. The detailed mathematical analysis can be obtained from the authors.

Results

The following information shows that the formation of intermediate compounds or complex ions might be expected in the molten binary system CsBr-CuBr.

From Table I it can be seen temperature coefficients, *b*, do not exhibit a smooth change from one pure component to the other. The same argument is true for the density data, Figure 1, where there is a discontinuity in the region of 0.6 mole fraction CsBr.

Figure 2 shows the positive deviation from additivity which increases with temperature and with well-defined maxima in the regions of 0.3 and 0.6 mole fractions CsBr at 950 °C. These maxima at the mentioned mole fractions also show up clearly in Figure 6 where the expansivities of the melt mixture are plotted vs. composition.

The volume increase on mixing (positive deviation from additivity) would thus indicate an increase in the amount of covalency. This argument is based on Klemm's (*5*) observation that, other things being equal, melts consisting of covalent molecules, because of weak intermolecular forces, have larger molar volumes than those of ionic melts possessing a strong Coulomb field of force. Positive deviations from additivity of the molar volumes are also observed with systems in which stable complex ions exist (*1*). Precise electrical conductivity and phase equilibrium data will be required for comparison to prove an increase in covalency and the existence of intermediate compounds or complex ions.

In Figures 3, 4, and 5 the plotted partial molar volumes can be compared with the molar volumes of the pure components. The maxima at about 0.6 mole fraction CsBr, that disappear with increasing temperature, coincide with the maxima observed in Figures 2 and 6.

Literature Cited

(1) Boardman, N. K., Dorman, F. H., Heyman, E., *J. Phys. Chem.*, **53**, 375 (1949).
(2) Brockris, J. O'M., Tomlinson, J. W., White, J. L., *Trans. Faraday Soc.*, **52**, 299 (1956).
(3) Hill, D. G. Cantor, S., Ward, W. T., *J. Inorg. Nucl. Chem.*, **29**, 241 (1967).
(4) Janz, G. J., "Molten Salts Handbook", Academic Press, New York, 1976, p 40.
(5) Klemm, W. Z., *Z. Anorg. Chem.*, **152**, 295 (1926).
(6) Lamprecht, Gert J., *J. Chem. Eng. Data*, **22**, 329 (1977).
(7) Moore, W. J., "Physical Chemistry", 5th ed., Longman, London, 1972, Chapter 7, p 235.
(8) Riebling, E. F., *J. Chem. Phys.*, **39**, 3022 (1963).

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Vapor-Liquid Equilibrium in the System 2-Propanol-Heptane

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New vapor-liquid data have been obtained for the binary system 2-propanol-heptane at 760 mmHg. The system presents strong deviations from ideal behavior and has a minimum boiling point azeotrope that boils at 75.7 °C and contains 62.5 mol % 2-propanol. The boiling points and activities have been correlated with the composition.

Introduction

Solutions of alcohols and hydrocarbons are known to deviate strongly from ideal behavior (*2*, *3*, *9*). For aromatic hydrocarbons the analysis of the thermodynamic and spectroscopic data has indicated the presence of an interaction between the π electrons and the proton of the hydroxyl group (*3*). Hwa and Ziegler (*2*) have proposed a more complicated model that assumes an additional interaction between the aromatic ring and alcohol polymer species which involves no breaking of hydrogen bonds. Van Ness et al. (*9*) have reported isothermal vapor-liquid equilibrium data as well as excess mixing properties for 2-propanol-heptane and several alcohol-hydrocarbon systems. This paper reports new isobaric vapor-liquid equilibrium data for the binary 2-propanol-heptane.

Table I. Physical Properties of Pure Compounds

index	compd	% purity GLC	refractive index at 25 °C	bp, °C (760 mmHg)
1	2-propanol	99.5[a]	1.3758[a] 1.3752[b]	82.3[a] 82.5[b]
2	heptane	99.7[a]	1.3858[a] 1.3851[b]	98.2[a] 98.4[b]

[a] Measured. [b] Reference 9.

Experimental Section

Purity of Materials. Analytical grade reagents purchased from Merck and Fluka were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

Apparatus and Procedure. An all-glass modified Dvorak and Boublik recirculation still (*1*) was used in the equilibrium determinations. The experimental features have been described previously (*10*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and an Autolab Model 6300 electronic integrator. The column was 200 cm long and 0.2 cm

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