J. Chem. Eng. Data **1984**, *29*, 375–379

Table III. Temperature Difference between Experimental and Calculated Values against Vapor Pressure Using Miller and Antoine Equations

	ΔT,[a] K	
P, kPa	Miller eq	Antoine eq
32.500	–0.14	–0.04
30.000	–0.06	–0.01
27.500	0.03	0.04
25.000	0.21	0.18
22.500	0.19	0.14
20.000	–0.10	–0.16
17.500	–0.14	–0.20
15.000	0.08	0.03
12.500	–0.04	–0.06
10.000	0.01	0.03
7.500	–0.06	0.00
5.000	–0.01	0.08
2.500	0.01	0.09
1.500	0.00	0.01
1.000	0.04	0.01
0.900	0.04	0.00
0.800	0.01	–0.03
0.700	0.05	0.01
0.650	0.01	–0.02
0.600	–0.08	–0.10
0.550	0.00	–0.02
0.500	–0.07	–0.06
0.450	–0.01	0.03
0.400	0.04	0.12

	Miller eq	Antoine eq
mean dif,[b] K	0.06	0.06
max dif,[a] K	0.21	–0.20

[a] $T = T_{\text{exptl}} - T_{\text{calcd}}$. [b] $\sum_i |T_{\text{exptl}} - T_{\text{calcd}}|_i / n$. n: number of data (=24).

Since the percent root mean square deviations of pressures (prms) using Chebyshev polynomials with the number of parameters from 3 to 10 were estimated as 2.70 at 3 parameters, 0.29 at 4 and 5, 0.26 at 6 and 7, 0.22 at 8–10, respectively, here 8 parameters are selected as written in Table II. The prms of the Miller and Antoine equations are listed as 0.29 and 0.33, respectively, in Table II. Percent pressure deviations and mean absolute deviations from the equations have also been presented in Table I.

Conversely, the temperatures were calculated by using the Miller and Antoine equations, and the differences between experimental and calculated values are shown in Table III. The mean differences of the temperatures obtained in both were equal to 0.06 K.

The Miller equation, having four constants, gave somewhat better correlations than the Antoine equation, having three constants, but the degrees of differences were very small.

Acknowledgment

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Glossary

p	pressure, kPa
T	temperature, K
t	*T* – 273.15 K

Greek Letters

ϵ	percent pressure deviation ($=100(P_{\text{exptl}} - P_{\text{calcd}})/P_{\text{exptl}}$)

Registry No. Tetralin, 119-64-2.

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Investigation of Vapor Pressures and Enthalpies and Entropies of Vaporization of Xanthene at Elevated Temperatures

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Vapor pressures (6.35–817.29 mmHg) of xanthene, a polynuclear aromatic (three-ring) compound containing an oxygen group, over the temperature range 423–589 K, were measured. The measurements were performed in a high-temperature static apparatus. Chebyshev polynomials have been used to fit the experimental vapor pressure data. The results have been further processed to evaluate the enthalpies of vaporization and compared with the predicted enthalpy values, by a recently developed generalized correlation which incorporates the renormalization group theory with the corresponding states principle. The entropies of vaporization were also evaluated at their respective temperatures for xanthene.

Introduction

Vapor pressures and enthalpies and entropies of vaporization are a few of the important physical properties required in designing coal-liquid and shale oil processing and separation plants. The thermodynamic properties are virtually unknown at high temperatures for the three-ring heavy polynuclear hydrocarbons. We reported previously (*1–3*) the vapor pressures of various condensed aromatic compounds. In this work we continue the measurements of vapor pressures of a three-ring, oxygen-containing, coal-derived liquid, xanthene. The vapor pressures of xanthene are reported over a wide range of temperatures up to the onset of thermal decomposition. No experimental vapor pressures or enthalpies of vaporization are

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Table I. Vapor Pressure and dp/dT of Xanthene

T, K	p, mmHg	dp/dT, mmHg K^{-1}	T, K	p, mmHg	dp/dT, mmHg K^{-1}
423.69	6.35	0.28	466.30	33.00	1.15
427.68	7.55	0.32	493.00	78.97	2.39
434.89	10.20	0.42	527.31	206.56	5.32
437.57	11.35	0.46	539.88	282.85	6.90
443.50	14.40	0.56	558.18	432.95	9.79
451.34	19.50	0.73	559.80	446.69	10.09
452.03	19.95	0.74	584.80	765.56	15.36
454.35	21.75	0.80	588.61	817.29	16.29
462.18	28.80	1.02			

reported in the literature in the range of the present investigation for xanthene. The experimental data of vapor pressures were fitted to Chebyshev polynomials and values of dp/dT were used to evaluate the enthalpies and hence entropies of vaporization of xanthene. A three-parameter corresponding states correlation developed by Sivaraman et al. (*4*, *5*) incorporating renormalization group theory (*6*) with the corresponding states principle (*7*) has been used to predict the enthalpies of vaporization of xanthene and compared with the present data evaluated by using experimental vapor pressures.

Experimental Section

Materials. Purity is an important factor in precise vapor pressure measurements. Samples of xanthene were purchased from Aldrich Chemical Co. with a purity of 99 mol %. The compound was further purified to a purity of 99.99 mol % by 48 passes in a zone refiner. The purities were checked by the freezing temperature method of Rossini et al. (*8*).

Apparatus and Procedure. In the present vapor pressure measurements a versatile high-temperature static apparatus developed by Sivaraman et al. (*2*) has been used. About 40 cm^3 of the purified sample was placed in the equilibrium cell. The procedures for degassing of the compound, attaining thermal equilibrium, and locating thermal degradation of the compound are the same as described earlier (*2*). The temperature (IPTS-68) near the cell was measured with an accuracy better than ±1 mK by means of a calibrated platinum resistance thermometer. The pressure measurements were made with a high-temperature Ruska differential pressure null detector and a calibrated Ruska digital quartz gauge (Model DDR 6000) with an accuracy better than ±0.01 mmHg.

Table II. Coefficients of Chebyshev Polynomials for T log (p/mmHg) for Xanthene[a]

A_0	2160.529
A_1	735.9533
A_2	−9.37571
A_3	0.578942
A_4	−0.300112
T_{max}, K	600.0
T_{min}, K	423.0
p_{rms}	0.53

[a] Fourth order.

Table III. Coefficients of Chebyshev Polynomial for T log (p/mmHg) for Xanthene[a,b]

A_0	3826.835
A_1	1481.981
A_2	−120.8118
A_3	−32.0658
A_4	−8.63591
T_{max}, K	833.0 K
T_{min}, K	423.0
p_{rms}	0.54

[a] Fourth order. [b] Inclusive of critical region.

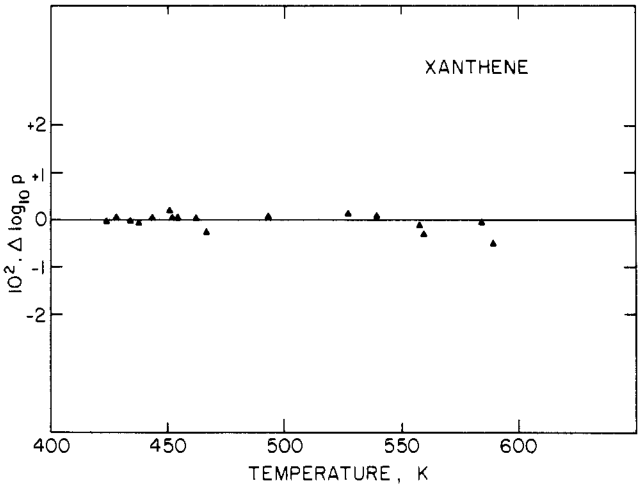

Figure 1. Residuals, Δ log (p/mm) = log (p_{exptl}/mm) − log (p_{calcd}/mm) for xanthene as a function of temperature.

Results and Discussion

Vapor pressures of xanthene were measured in the temperature range 423.69–588.61 K. The values of experimental vapor pressures of xanthene at various temperatures and their respective dp/dT are listed in Table I. Chelyshev polynomials (*9*) of the following form have been used for representation of the vapor pressure curves of xanthene studied:

$$T \log p = \tfrac{1}{2}a_0 + a_1E_1(x) + a_2E_2(x) + \ldots + a_sE_s(x) + \ldots + a_nE_n(x) \quad (1)$$

where $E_s(x) = \cos(s \cos^{-1} x)$ is the Chebyshev polynomial in x of degree s, and where x is a function of temperature, varying between the limits 1 and −1. The first few Chebyshev polynomials are $E_1(x) = x$, $E_2(x) = 2x^2 - 1$, $E_3(x) = 4x^3 - 3x$ and are evaluated from the equation

$$E_{s+1}(x) - 2xE_s(x) + E_{s-1}(x) = 0$$

in which x is defined as

$$x = \{2T - (T_{max} + T_{min})\}/(T_{max} - T_{min}) \quad (2)$$

where T_{max} and T_{min} are temperatures, respectively, just above and just below the extreme temperatures of the measured values. p_{rms} is the percent root mean square deviation in pressure defined as

$$p_{rms} = (\{\textstyle\sum[100(p_{exptl} - p_{calcd})/p_{exptl}]^2\}/n)^{1/2} \quad (3)$$

The values of T log (p/mmHg) were fitted by Chebyshev polynomials up to degree $i = 4$. The coefficients of the polynomials cover the temperature ranges bounded by T_{max} and T_{min} given in Table II. For xanthene a fourth-order polyminal was chosen to give 0.53% root mean square deviation in pressure. In Figure 1 the residuals, Δ log (p_{exptl}/mmHg) − log (p_{calcd}/mmHg) are presented for xanthene for various temperatures.

Since xanthene was thermally unstable above 590 K, we could not continue our vapor pressure measurements beyond 588.61 K. The boiling temperature (584.3 K) was obtained from the present experimental vapor pressure data. The critical parameters T_c and p_c for xanthene were estimated by Lydersons method (*10*), which employs structural contributions (T_c = 833.0 K; p_c = 29.3 atm). Although the vapor pressure measurements were not possible up to critical temperature, the present vapor pressure data were fitted over an extended range of temperature including the estimated critical temperature (T_c). An extrapolation of this sort will be quite useful for chemical engineering purposes. A fourth-order polynomial gave a reasonable fit with root mean square deviations of pressure (p_{rms})

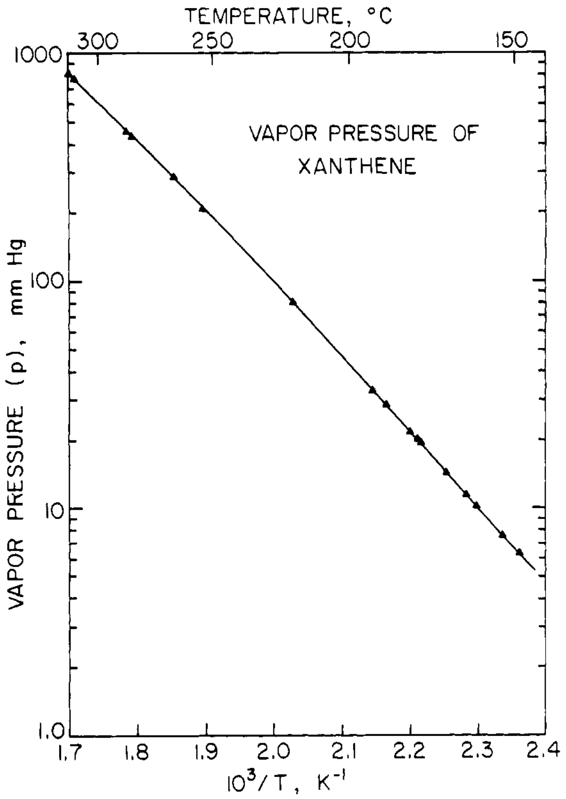

Figure 2. Vapor pressures of xanthene.

being 0.54% for xanthene. The respective coefficients of the polynomials are given in Table III. Present vapor pressure measurements in liquid xanthene are in the region 423.69–588.61 K and are shown in Figure 2. Although no vapor pressure values are reported in the literature in the range of the present investigation, the boiling point value (584.3 K) determined from our experimental data is quite comparable to the one reported (588.15 K) elsewhere (*11*).

Enthalpy of Vaporization. Enthalpies of vaporization of xanthene were calculated from the Clapeyron equation via

$$dp/dT = L/[(RT^2/p)\Delta z] \qquad (4)$$

where $\Delta z = z^{\mathrm{v}}_{\mathrm{sat}} - z^{\mathrm{l}}_{\mathrm{sat}}$, the difference between the compressibility factors of the saturated vapor and liquid, L is the enthalpy of vaporization, p is the vapor pressure, and T is the temperature.

Pitzer's three-parameter corresponding states correlation has been used to calculate the compressibility factors of saturated liquid and vapor:

$$z = z^{(0)} + \omega z^{(1)} \qquad (5)$$

where $z^{(0)}$ is the compressibility factor for a simple fluid, $z^{(1)}$ is the compression factor for the deviation from a simple fluid, and ω is the acentric factor given by

$$\omega = -\log p_{\mathrm{r}} - 1.0 \qquad (6)$$

The reduced vapor pressure p_{r} equals p/p_{c} at reduced temperature $T_{\mathrm{r}} = T/T_{\mathrm{c}} = 0.7$. For xanthene, ω is calculated ($\omega = 0.478$) from the experimental vapor pressures. Pitzer's values of $z^{(0)}$ and $z^{(1)}$ for either saturated vapor or liquid as a function of reduced temperature $T_{\mathrm{r}} = 0.56$ and $T_{\mathrm{r}} = 0.94$ were calculated by means of a polynomial given by

$$y = A_0 + A_1T_{\mathrm{r}} + A_2T_{\mathrm{r}}^2 + A_3T_{\mathrm{r}}^3 + A_4T_{\mathrm{r}}^4 \qquad (7)$$

The coefficients of the polynomial are given in Table IV. If one knows dp/dT, Δz, and p at various temperatures, the enthalpies of vaporization can be calculated from eq 4; they are listed in Table V at 10 K intervals and are shown in Figure 3.

Table IV. Coefficients of Polynomial for Compressibility Factors $z^{(0)}$ and $z^{(1)}$ for Saturated Vapor and Liquid at Reduced Temperature Ranges between $T_{\mathrm{r}} = 0.94$ and $T_{\mathrm{r}} = 0.56$

	vapor		liquid	
coeff	$z^{(0)}$	$z^{(1)}$	$z^{(0)}$	$z^{(1)}$
A_0	1.0329	4.8701	0.8930	−0.3242
A_1	−0.5760	−25.4854	−5.2910	1.5098
A_2	1.7942	48.1356	11.7974	−2.1798
A_3	−1.7863	−37.6756	−11.8799	0.8856
A_4		10.1178	4.673	

Table V. Comparison of Experimental and Predicted Enthalpies of Vaporization (kJ mol^{-1}) for Xanthene

T, K	L_{exptl}	L_{calcd}	error, %
425.15	65.5	65.6	0.15
435.15	64.5	65.0	0.78
445.15	63.7	64.3	0.94
455.15	62.9	63.7	1.27
465.15	62.2	63.0	1.35
475.15	61.5	62.4	1.46
485.15	60.9	61.7	1.31
495.15	60.3	61.0	1.16
505.15	59.7	60.3	1.01
515.15	59.2	59.6	0.68
525.15	58.6	58.9	0.51
535.15	58.0	58.2	0.34
545.15	57.4	57.5	0.17
555.15	56.7	56.6	−0.18
565.15	56.1	55.9	−0.36
575.15	55.2	55.1	−0.18
585.15	54.4	54.3	−0.18

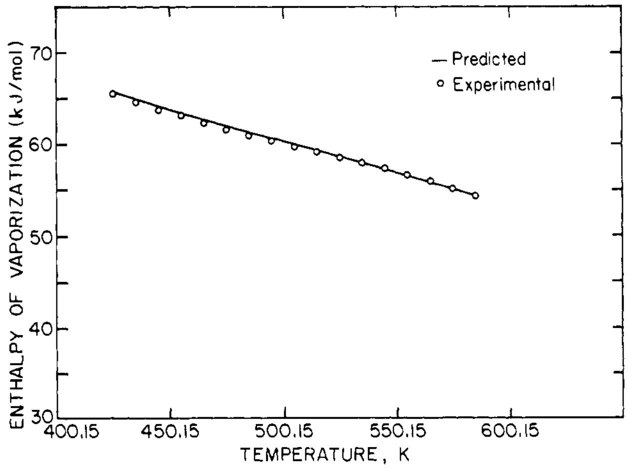

Figure 3. Enthalpy of vaporization of xanthene as a function of temperature. Solid line denotes the predicted values and black circles the present data.

The estimated accuracy is ±1.5 kJ mol^{-1}.

Comparison with Correlation Data. No experimental enthalpies of vaporization for xanthene, a high molar mass compound, are available for comparison at these elevated temperatures. However, a generalized two-parameter correlation which incorporates the renormalization group theory with the corresponding states principle, developed by Sivaraman et al. (*4*, *5*), has been used to predict the enthalpies of vaporization of xanthene at various measured temperatures. According to that model, the dimensionless enthalpies of vaporization

$$L^* = L^*_{(0)} + \omega^* L_{(1)} \qquad (8)$$

where

$$L^* = L/RT_{\mathrm{c}} \qquad L^*_{(0)} = L_{(0)}/RT_{\mathrm{c}}$$
$$L^*_{(1)} = L_{(1)}/RT_{\mathrm{c}} \qquad (9)$$

$$\omega^* = \omega/\omega_1 \qquad (10)$$

Table VI. Coefficients of Least-Squares Analysis

a. $L^*_{(0)}$ Using Eq 11	
A_1	−0.93298
A_2	275.553255
A_3	416.646872
B_1	−617.767986
B_2	−94.438858
B_3	29.557315
b. $L^*_{(1)}$ Using Eq 12	
A_1^*	10.494541
A_2^*	−351.097613
A_3^*	−617.139173
B_1^*	854.731448
B_2^*	155.934841
B_3^*	−50.592504

Table VII. Entropy of Vaporization (kJ mol^{-1} K^{-1}) of Xanthene

T, K	ΔS	T, K	ΔS
425.15	0.1541	515.15	0.1149
435.15	0.1482	525.15	0.1116
445.15	0.1431	535.15	0.1084
455.15	0.1382	545.15	0.1053
465.15	0.1337	555.15	0.1021
475.15	0.1295	565.15	0.0993
485.15	0.1255	575.15	0.0960
495.15	0.1218	585.15	0.0930
505.15	0.1182		

R is the gas constant (8.3145 J mol^{-1} K^{-1}); T_c is the critical temperature of xanthene (kelvin); ω is the acentric factor; ω_1 = 0.490; p_c is the critical pressure; $L^*_{(0)}$ and $L^*_{(1)}$ are the reduced enthalpy of vaporization taking into consideration its singular (near critical) and analytic background contributions (*12*) as

$$L^*_{(0)} = A_1\epsilon^{\beta} + A_2\epsilon^{\beta+\Delta} + A_3\epsilon^{1-\alpha+\beta} + B_1\epsilon + B_2\epsilon^2 + B_3\epsilon^3 \tag{11}$$

$$L^*_{(1)} = A_1^*\epsilon^{\beta} + A_2^*\epsilon^{\beta+\Delta} + A_3^*\epsilon^{1-\alpha+\beta} + B_1^*\epsilon + B_2^*\epsilon^2 + B_3^*\epsilon^3 \tag{12}$$

where

$$\epsilon = (T_c - T)/T_c \tag{13}$$

α, β, Δ are critical exponents given by $\alpha = {}^1/_8$, $\beta = {}^1/_3$, $\Delta = {}^1/_2$ (Wegner's first "gap" exponent), obtained from renormalization group theoretical calculations. The system-independent, generalized coefficients A_1, A_2, A_3, B_1, B_2, B_3, A_1^*, A_2^*, A_3^*, B_1^*, B_2^*, and B_3^* in eq 11 and 12 are listed in Table VI, a and b.

These values were substituted to calculate the predicted enthalpy of vaporization, L_{calcd}, for xanthene. These predicted enthalpy data and the data obtained through experimental vapor pressures were given in Table V for comparison. Our present results are in good agreement with the predicted ones. The comparison yielded the percent root mean square deviation

$$L_{\text{rms}} = ([\textstyle\sum\{100(L_{\text{exptl}} - L_{\text{calcd}})/L_{\text{exptl}}\}^2]/n)^{1/2}$$

for xanthene as 0.82. The percent residual enthalpies of vaporization have been plotted against their respective temperatures for xanthene in Figure 4. Entropy of vaporization was calculated from

$$\Delta S_v = L/T \tag{14}$$

at various temperatures for xanthene and are presented in Table VII. The variation of entropy of vaporization with temperature is shown in Figure 5.

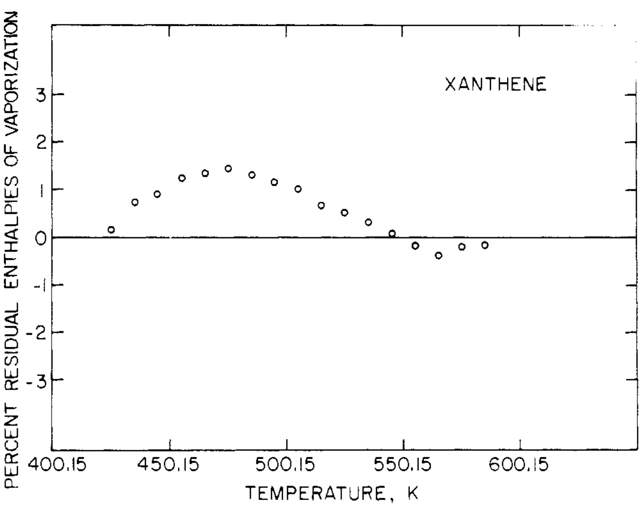

Figure 4. Percent residual enthalpies of vaporization at various temperatures for xanthene.

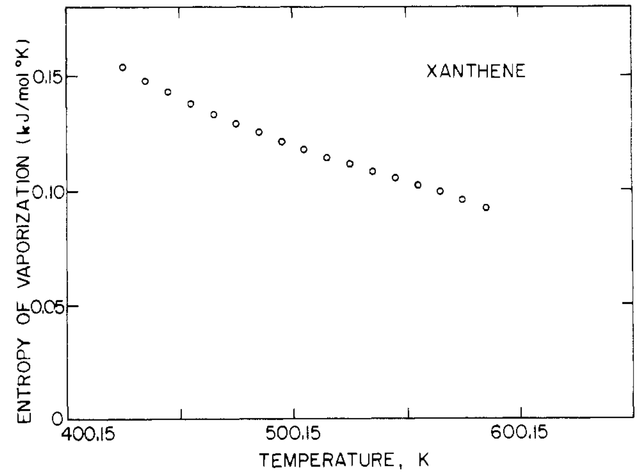

Figure 5. Entropy of vaporization of xanthene as a function of temperature.

Acknowledgment

We thank Mr. Dave Morgan for his assistance in purifying the compound.

Appendix

Example. Calculate the enthalpy of vaporization for xanthene at 525.15 K.

Solution. Xanthene. Critical temperature T_c = 833.0 K; ω = 0.478. From eq 13

$$\epsilon = (T_c - T)/T_c = (833.0 - 525.15)/833.0 = 0.3696$$

From eq 11 and 12

$$L^*_{(0)} = 4.9783$$

$$L^*_{(1)} = 3.6167$$

From eq 10

$$\omega^* = 0.478/0.490 = 0.9755$$

$$L^* = L^*_{(0)} + \omega^* L^*_{(1)} = 8.5064$$

$$L = L^* R T_c = (8.5064)(8.3145)(833.0) = 58.9 \text{ kJ mol}^{-1}$$

From the present experimental vapor pressure measurements

$$L = 58.6 \text{ kJ mol}^{-1}$$

The error is 0.30 or 0.51%.

Registry No. Xanthene, 92-83-1.

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Densities of Aqueous Solutions of 18 Inorganic Substances

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Densities of aqueous solutions of $Cd(NO_3)_2$, $Co(NO_3)_2$, H_2SiF_6, $K_3Fe(CN)_6$, $KMnO_4$, KNO_2, $Mg(ClO_4)_2$, NaH_2PO_4, Na_2HPO_4, Na_2MoO_4, Na_3PO_4, $Na_4P_2O_7$, Na_2SO_3, $Na_2S_2O_3$, Na_2WO_4, $NH_4Al(SO_4)_2$, $(NH_4)_2C_2O_4$, and NH_4CH_3COO for temperatures from 5 to 85 °C and concentrations up to near saturation determined pycnometrically are reported.

Introduction

The densities of aqueous solutions are frequently used in both physical chemistry and chemical engineering. In the latter case they are necessary in establishing material balance of a process using solutions as a medium and/or volume of technological equipment. For purposes of chemical engineering it seems advantageous when concentration and temperature dependence of solution density is represented by a single equation valid in the range 0–100 °C and up to saturation concentration.

Also reliable data covering the whole interval of concentrations and temperatures should be available in sufficient supply. Since for many inorganic systems data reported in the literature are restricted to a rather narrow temperature and concentration range, we have measured missing densities for 18 systems.

Theoretical Section

The apparent molar volume of solute in a binary solution is defined as (*1*)

$$\phi_V = (V - n_1 V_{m,1})/n_2 = \frac{1}{n_2}\left[\frac{n_1 M_1 + n_2 M_2}{\rho} - \frac{n_1 M_1}{\rho_1}\right] \tag{1}$$

for constant temperature and pressure. If the solution composition is expressed by the number of moles of solute in 1 m^3 of solution, i.e., $n_2 = c$, $n_1 = (\rho - cM_2)/M_1$, then eq 1 acquires the form

$$\phi_V = (\rho_1 - \rho)/c\rho_1 + M_2/\rho_1 \tag{2}$$

Combination of eq 2 with the relation after Masson (*2*)

$$\phi_V = \phi_V{}^\circ + s_{\text{exptl}} c^{1/2} \tag{3}$$

gives

$$\rho = \rho_1 + \alpha c - \beta c^{3/2} \tag{4}$$

where

$$\alpha = M_2 - \rho_1 \phi_V{}^\circ \tag{5}$$

$$\beta = s_{\text{exptl}} \rho_1 \tag{6}$$

Relation 4 describes the dependence of solution density on concentration at constant temperature. Introducing the temperature dependence of α and β in the form

$$\alpha(t) = A + Bt + Ct^2 \tag{7}$$

$$\beta(t) = -(D + Et + Ft^2) \tag{8}$$

into eq 4 and rearranging gives

$$\rho(t) = \rho_1(t) + Ac + Bct + Cct^2 + Dc^{3/2} + Ec^{3/2}t + Fc^{3/2}t^2 \tag{9}$$

Relation 9 describing the concentration–temperature dependence of densities of binary aqueous solutions can thus be regarded as theoretically justified. Its application to aqueous binary solutions has been tested for over 300 systems and found very satisfactory (*3*). Moreover, the physical parameter of solute, $\phi_V{}^\circ$, calculated from constants of eq 9, is rather close to the theoretical values (*4*). Equation 9 can also be used for the estimation of the ternary system densities on the basis of data for binary systems (*5*).

Relations proposed in the literature for the description of the concentration and temperature dependences of densities of aqueous solutions are mostly of an empirical nature, e.g., ref *6–10*. Such equations have, however, several disadvantages compared with eq 9, mainly (i) narrower field of application due to their validity for either concentration or temperature dependence, (ii) less satisfactory description of the density depen-

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