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INVESTIGATION OF THE SPECIFIC HEAT AT CONSTANT PRESSURE OF MUTUAL SOLUTIONS OF METHYL AND ISOPROPYL ALCOHOLS AT DIFFERENT TEMPERATURES AND PRESSURES

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Results of investigation of the specific heat at constant pressure of binary solutions of methyl and isopropyl alcohols as a function of temperature, pressure, and concentration are given. The empirical equation of the concentration dependence of the specific heat at constant pressure of a methanol–propanol 2 system is proposed.

Investigation of the thermodynamic properties of aliphatic alcohols and their solutions in a wide interval of temperatures and pressures is a topical problem of modern thermophysics.

A number of works carried out recently are devoted to studying the calorific properties of individual pure alcohols of normal and isostructure. Investigations of the specific heat at constant pressure (c_p) of atmospheric-pressure normal alcohols are reviewed in detail in [1, 2] with indication of the temperature interval and the experimental method. The analysis of these data shows that the experimental works cover a fairly wide range of temperatures for *n*-alcohols with a carbon number of C_1 to C_{18}. Experimental investigations of c_p of *n*-alcohols, which have been carried out at different pressures, are reviewed in [3]. However, works carried out at high pressures are few in number, and those devoted to measuring the specific heat at constant pressure of mutual solutions of aliphatic alcohols are still fewer. Data on c_p of methanol solutions with other alcohols are entirely absent in the literature. Therefore, in the present work we sought to study the specific heat of methanol–isopropanol solutions. The experiments were conducted for three mass concentrations (25, 50, and 75%) and in the interval of temperatures 298–525 K and pressures 0.101–50 MPa.

The measurements of c_p' have been carried out on a setup with a pulse-periodic regime [4, 5]. The dimensions of the measuring cell were as follows: length of the ampoule 137 mm, outside diameter 30 mm, inside diameter 28 mm, and gap between the ampoule and the autoclave 1.5 mm.

To prepare the solutions we used chemically pure methanol ("KhCh" grade) (CH_3OH) and isopropanol (C_3H_7OH) with a degree of purity of 99.5 and 99.6% respectively with the following characteristics: ρ_4^{20} = 791.15 kg/m^3, n_D^{20} = 1.3288, T_{boil} = 337.70 K, and T_{cr} = 512.64 K for methanol and ρ_4^{20} = 785.2 kg/m^3, n_D^{20} = 1.3773, T_{boil} = 355.39 K, and T_{cr} = 508.30 K for isopropanol.

The experiments have been conducted according to the isotherms. The temperature measurement step was about 25 K. The volumetric specific heat at constant pressure was measured at pressures of 0.101, 5, 10, 20, 30, 40, and 50 MPa.

The volumetric specific heat at constant pressure of the solutions was calculated according to the experimental data from the equation [4, 5]

$$c_p' = \left[\frac{W(1-k)}{b_0} - M_{\text{b}}c_{\text{b}}\right]\left[V\left(1+\frac{2\delta}{3R}+\frac{2\delta'}{3l}\right)\right]^{-1} . \tag{1}$$

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TABLE 1. Experimental Values of the Volumetric Specific Heat at Constant Pressure of Methanol and Isopropanol Solutions at Different Pressures and Temperatures

T	p, MPa						
	0.101	5	10	20	30	40	50
25% methanol + 75% isopropanol							
298.4	2015	2017	2020	2028	2035	2039	2042
319.7	2203	2202	2201	2198	2195	2193	2190
344.1	2377	2370	2361	2352	2342	2336	2326
370.5		2516	2492	2475	2464	2456	2446
397.2		2616	2580	2564	2553	2544	2534
420.8		2675	2637	2615	2608	2596	2593
446.6		2716	2687	2635	2629	2614	2619
471.3		2738	2736	2628	2621	2608	2617
504.2			2762	2584	2583	2577	2595
50% methanol + 50% isopropanol							
298.6	2007	2010	2014	2023	2030	2034	2036
321.3	2162	2163	2160	2159	2155	2150	2143
342.2	2301	2293	2281	2272	2260	2252	2241
369.5		2442	2412	2396	2379	2368	2357
395.1		2555	2517	2495	2474	2459	2448
420.0		2659	2610	2573	2550	2527	2524
448.2		2780	2731	2637	2607	2581	2583
472.4		2897	2885	2677	2641	2614	2622
503.1				2701	2662	2644	2661
75% methanol + 25% isopropanol							
300.1	2000	2005	2010	2017	2016	2014	2013
320.4	2103	2107	2106	2105	2095	2091	2083
340.2	2206	2203	2194	2188	2173	2163	2153
376.8		2380	2348	2330	2305	2288	2278
400.1		2495	2444	2419	2386	2362	2353
426.3		2645	2576	2513	2472	2440	2437
450.7		2810	2749	2596	2544	2504	2506
470.6		2995	2993	2661	2595	2554	2560
502.4				2743	2665	2636	2642

Prior to the main experiment, we carried out check measurements using the model liquid–methanol. The maximum error of experimental data in the investigated range of state variables amounted to 2.2%. It turned out to be impossible to compute the mass specific heat (c_p) on the basis of the experimental volumetric specific heat (c'_p) for the methanol–isopropanol solutions because of the absence of literature data on the density of the system indicated.

The pressure in the experiments was produced and measured by an MP-600 dead-end pressure-gauge tester (accuracy class 0.05), while the temperature was maintained by a three-section electric furnace and was measured by a PTS-10 platinum standard resistance thermometer with an error of ±0.05 K.

The results of measuring the volumetric specific heat at constant pressure of the methanol–isopropanol system are summarized in Table 1.

To supplement and generalize the experimental data obtained we employed the literature data on c'_p of pure metals and isopropanol [6] that had been obtained experimentally on an identical setup by the method of pulse-period regime, which enabled us to automatically eliminate a systematic error in establishing the concentration dependence of c'_p. As is clear from the table, the concentration dependence of the volumetric specific heat at constant pressure deviates from the additivity law in the direction of negative values at moderate temperatures and in the direction of positive values at high temperatures. The deviation is scarcely affected by pressure; a pressure increase contributes to the decrease in $\delta c'_p$ from the additivity line. Thus, for example, whereas the maximum deviation is $\delta c'_p = c'_p - c'_{padd} = -13$ kJ/(m^3·K) and $\delta c'_p/c'_{padd} = -0.63\%$ for a concentration of (50 + 50)%, $T = 303$ K, and $p = 0.101$ MPa, it is $\delta c'_p = -15$ kJ/(m^3·K) and $\delta c'_p/c'_{padd} = -0.73\%$ even at $T = 303$ K and $p = 50$ MPa, $\delta c'_p = 161.5$ and $\delta c'_p/c'_{padd} = 6.4\%$ at $T = 523$ K and $p = 20$ MPa, and $\delta c'_p = 160$ and $\delta c'_p/c'_{padd} = 6.45\%$ at $T = 523$ and $p = 50$ MPa.

An analogous situation is observed for a concentration of (25 + 75)% and (75 + 25)%.

The data obtained on c'_p of the solutions as a function of p, T, and x are described by a concentration equation of the form

$$c'_p = c'_{p1}x_1 + c'_{p2}x_2 + x_1x_2\,(\alpha\Delta T - \beta p + \gamma)\,, \tag{2}$$

where

$$\Delta T = T - T_0\,; \quad T_0 = (T_{\mathrm{boil1}} + T_{\mathrm{boil2}})/2\,.$$

The values of the coefficients appearing in Eq. (2) have been found based on experimental data and are equal to $\alpha = 3.186$, $\beta = 0.16$, and $\gamma = 86.467$. The maximum error throughout the interval investigated amounts to ±0.9%.

It is of interest to establish the interrelation between the volumetric specific heat at constant pressure and the thermal conductivity of solutions of monobasic alcohols. In this work, consideration is given to the dependence $c'_p = f(\lambda)$ for methanol–isopropanol solutions at different temperatures and pressures and with constant concentrations. The values of λ of the solution have been borrowed from [7]. We have carried out such processing of experimental data for pure *n*-undecyl and *n*-dodecyl alcohols in [8, 9].

For generalization of the dependence $c'_p = f(\lambda)$ we can propose a single two-parameter equation of the form

$$c'_p = c'^{*}_p + c'^{**}_p\,, \quad c'^{*}_p = A + B\lambda\,, \quad c'^{**}_p = E + Dp\,. \tag{3}$$

Based on the experimental results obtained we have found the coefficients of Eq. (3) by the least-squares method: $A = 5990.435$, $B = -25{,}217.4$, $E = -0.739$, and $D = 14.4$.

Thus, Eq. (3) yields

$$c'_{p0.5} = 5989.696 - 25217.4\lambda + 14.4p\,. \tag{4}$$

Equation (4) describes the entire array of experimental data on the methanol–isopropanol system ($x_1 = x_2 = 0.5$) with a maximum error of 3.5%.

Equation (3) can be employed for extrapolation and interpolation computations and for precomputation of c'_p of the solutions.

NOTATION

c_p, mass specific heat at constant pressure, kJ/(kg·K); c'_p, volumetric specific heat at constant pressure, kJ/(m^3·K); V, volume of the substance under study, m^3; $k = W_{\mathrm{loss}}/W$, coefficient allowing for the heat loss; W, internal-heater power, kW; W_{loss}, required correction for the heat loss, kW; $b_0 = b[1 + 1/12(\Delta t^2/\theta^2_{\max})]$, rate of heating at a given temperature, K/sec; $b = \Delta t/\Delta\tau$; $\theta_{\max}$, maximum temperature difference in the ring layer; $M_\mathrm{b}c_\mathrm{b}$, total ballast heat capacity of the ampoule, kJ/K; δ and δ', thickness of the ring and end plane liquid layers, respectively, lying between the cylindrical ampoule and the interior wall of the skeleton, m; R_1 and l, radius and length of the ampoule, m; p, pressure, MPa; T, absolute temperature, K; T_0, basic temperature, K; T_{boil1} and T_{boil2}, boiling temperature of the first and second components, K; x_1 and x_2, concentrations of the first and second components, wt. fractions; c'_{p1} and c'_{p2}, volumetric specific heats at constant pressure of the first and second components, $\delta c'_p$, deviation from the additivity rule; α, β, and γ, constant coefficients of Eq. (2) for the given system; c'_{add}, value of the volumetric specific heat at constant pressure of the solutions on the additivity line; $c'_{p0.5}$, value of the volumetric specific heat at constant pressure of the solutions for $x_1 = x_2 = 0.5$; λ, thermal conductivity of the solution, W/(m·K). Subscripts: add, additivity; boil, boiling; cr, critical; loss, loss; b, ballast; 0, initial value; max, maximum.

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