EXPERIMENTAL STUDY OF HEAT CAPACITIES OF DILUTE AQUEOUS SOLUTIONS OF NONELECTROLYTES

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Heat capacities of the following solutions are measured over the temperature range 273-320°K and concentration range 0-0.01 molar ketone: water–methyl ethyl ketone, water–methyl butyl ketone, water–methyl isobutyl ketone.

Very little is known of the nature of structural changes occurring in water under the influence of dissolved molecules. Recently, interest in the study of dilute aqueous solutions of nonelectrolytes has increased greatly in connection with the unique properties of pure water, which prove to have a significant effect on the properties of the solutions.

A wide range of experimental material on aqueous solutions of alcohols is available in the literature [1]. Ketones, like alcohols, are nonelectrolytes. Although quite similar to alcohols, they differ from the latter in the absence of association (hydrogen-bond formation) in the pure liquid ketones [2] and in the nature of the polar group, i.e., in the strength and number of hydrogen bonds which they form with water. It is natural to expect that the effect of water will be strongest in dilute solutions. At low concentrations of the nonelectrolyte in water, the characteristic hydrogen-bond structure of the latter will be retained.

There exists a well-known "iceberg" theory or hypothesis of "water structuring by nonelectrolytes" put forward by Frank and Evans [3], according to which the water molecules form an ice-like structure around the molecules of the dissolved nonelectrolyte. Thus, the structure of the water is changed by the dissolved nonelectrolyte. This fact cannot help but be reflected in the thermodynamic properties of the water–nonelectrolyte system, in particular, in such a significant property as the heat capacity of the solution.

It follows from review [4] that the heat capacity of dilute aqueous solutions of alcohols is dependent on concentration in a quite complex manner. The experimental data of a number of authors were presented in [4]. It was suggested that adjustment of the alcohol molecule into the water structure occurs up to some critical concentration which corresponds to the maximum heat capacity, after which ordering in the solution is gradually lost. The existence of some ordering-type phase transition in the solution was proposed.

The experimental data presented in [5, 6] are interesting in the same sense. In these studies λ-anomalies in heat capacity were observed in dilute solutions of water–tertiary butanol and water–polyethylene oxide.

Experimental studies of the thermodynamic properties of dilute aqueous solutions of nonelectrolytes are quite cumbersome, so that at the present there is an insufficient quantity of data for analysis and generalization. The studies of heat capacity whose results are presented in the present paper were performed with an adiabatic calorimetric apparatus prepared by the Khabarovsk Filial of the All-Union Scientific-Research Institute of Physicotechnical and Radiotechnical Measurements. The apparatus and basic technique used are described in [7]. Some changes were made in the construction of the measurement cell (calorimeter. The calorimeter was sealed with a brass flange. The heater was a Constantan wire, bifilar wound on a silvered copper capillary twisted into a spiral. The capillary is located inside the calorimeter along the axis of the latter, accurately centered. Location of the heater in such a position ensures sufficiently rapid establishment of thermodynamic equilibrium in the calorimeter–specimen system.

The uncertainty in measurement of the temperature dependence of heat capacity is estimated to be 0.2-0.3%, while the uncertainty in the concentration dependence is 0.5-0.6%. The

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TABLE 1. Experimental Data on Heat Capacities of Binary Water–Ketone (x_2) Solutions

T_1, °K	T_2, °K	ΔT, °K	T_m, °K	τ, sec	Q, J	mc, J/°K	$m_c c_c$, J/°K	C_{sp}, J/g·°K
Water–methyl ethyl ketone								
$x_2=0$								
277,38	281,86	4,48	279,62	2400	422,856	94,388	14,525	4,199
291,27	295,74	4,47	293,51	»	420,485	94,068	14,628	4,177
295,75	300,22	4,47	297,99	»	420,596	94,093	14,663	4,177
300,22	304,69	4,47	302,46	»	420,612	94,097	14,698	4,175
306,64	311,09	4,45	308,87	»	418,818	94,116	14,747	4,174
316,33	320,76	4,43	318,55	»	417,176	94,171	14,821	4,173
319,19	323,63	4,44	321,41	»	418,332	94,219	14,843	4,174
$x_2=0{,}003$								
277,43	282,20	4,77	279,82	3600	451,114	94,573	14,546	4,192
282,20	286,97	4,77	284,59	»	450,511	94,447	14,582	4,183
286,98	291,74	4,76	289,36	»	450,369	94,615	14,619	4,190
289,29	294,04	4,75	291,67	»	448,979	94,522	14,637	4,184
300,44	305,18	4,74	302,81	»	447,491	94,407	14,722	4,174
305,19	309,94	4,75	307,57	»	448,171	94,352	14,759	4,169
309,95	314,69	4,74	312,32	»	447,529	94,415	14,795	4,170
$x_2=0{,}006$								
283,87	286,35	2,48	285,11	1800	232,719	93,838	14,569	4,200
287,97	291,50	3,53	289,74	3600	330,452	93,613	14,605	4,186
301,80	306,56	4,76	304,18	3600	445,126	93,514	14,716	4,175
305,17	309,92	4,75	307,55	»	444,499	93,579	14,742	4,177
309,93	314,68	4,75	312,31	»	444,634	93,607	14,779	4,177
314,75	319,44	4,69	317,10	»	438,866	93,575	14,815	4,173
$x_2=0{,}007$								
277,23	281,93	4,7	279,58	3600	453,662	96,524	14,521	4,259
281,93	286,65	4,72	284,29	»	453,588	96,099	14,564	4,235
293,12	297,82	4,70	295,47	»	451,929	96,155	14,650	4,233
297,82	302,51	4,69	300,17	»	451,368	96,241	14,686	4,236
305,47	307,82	2,35	306,65	1800	225,743	96,061	14,735	4,224
305,94	310,63	4,69	308,29	3600	451,382	96,244	14,748	4,233
$x_2=0{,}008$								
277,20	280,38	3,18	278,79	2400	303,308	95,380	14,5380	4,280
288,03	291,35	3,32	289,69	2400	315,198	94,939	14,605	4,253
291,76	296,51	4,75	294,144	3600	450,694	94,883	14,639	4,248
296,52	299,70	3,18	298,11	2400	301,600	94,843	14,670	4,244
305,82	308,19	2,37	307,01	1800	224,709	94,814	14,738	4,239
308,20	312,97	4,77	310,59	3600	452,359	94,834	14,766	4,239
312,97	317,71	4,74	315,34	3600	449,532	94,838	14,802	4,237
$x_2=0{,}009$								
277,60	282,44	4,84	280,02	3600	458,170	94,663	14,536	4,207
282,44	287,28	4,84	284,86	»	457,750	94,577	14,574	4,201
292,46	297,30	4,84	294,88	»	456,256	94,268	14,651	4,180
302,51	307,34	4,83	304,93	»	455,806	94,370	14,728	4,182
307,34	312,16	4,82	309,75	»	455,230	94,446	14,765	4,184
312,18	316,99	4,81	314,59	»	454,550	94,501	14,799	4,185
$x_2=0{,}01$								
276,93	281,68	4,75	279,31	3600	448,971	94,520	14,531	4,198
281,70	286,46	4,76	284,08	»	448,942	94,316	14,562	4,186
291,38	296,11	4,73	293,75	»	444,790	94,036	14,636	4,167
296,13	300,89	4,76	298,51	»	447,653	94,045	14,673	4,166
300,41	305,17	4,76	302,79	»	447,403	93,992	14,706	4,161
305,18	309,93	4,75	307,56	»	447,099	94,126	14,743	4,166
309,96	314,71	4,75	312,34	»	446,352	93,969	14,779	4,156

TABLE 1 (Continued)

T_1, °K	T_2, °K	ΔT, °K	T_m, °K	τ, sec	Q, J	mc, J/°K	$m_c c_c$, J/°K	C_{sp}, J/g·°K
				Water– methyl butyl ketone				
				$x_2=0,004$				
277,07	281,60	4,53	279,34	2400	432,160	95,400	14,517	4,235
289,68	249,19	4,51	291,94	»	430,195	95,387	14,617	4,229
290,60	293,98	3,38	292,29	1800	322,087	95,292	14,620	4,224
204,20	298,69	4,49	296,45	2400	429,238	95,599	14,651	4,239
309,66	314,12	4,46	311,89	2400	426,245	95,771	14,770	4,241
314,13	317,46	3,33	315,80	1800	320,406	96,218	14,800	4,263
				$x_2=0,005$				
278,34	282,93	4,59	280,64	2400	430,730	93,841	14,548	4,239
289,64	293,08	3,44	291,36	1800	322,298	93,691	14,614	4,228
296,02	300,59	4,57	298,31	2400	428,077	93,671	14,667	4,224
300,61	305,17	4,56	302,89	»	427,355	93,718	14,720	4,224
305,19	309,74	4,55	307,47	»	426,138	93,657	14,737	4,219
310,48	315,00	4,52	312,74	»	423,786	93,758	14,777	4,223
315,01	319,53	4,52	317,27	»	424,090	93,825	14,813	4,224
				$x_2=0,006$				
276,59	281,12	4,53	278,86	2400	428,841	94,667	14,521	4,250
281,13	285,65	4,52	283,39	2400	428,291	94,755	14,551	4,253
285,66	290,63	4,97	288,15	2640	471,006	94,770	14,588	4,252
293,10	297,64	4,54	295,37	2400	429,326	94,565	14,643	4,238
297,66	302,20	4,54	299,93	»	428,917	94,475	14,678	4,231
307,65	312,17	4,52	309,91	»	427,464	94,572	14,755	4,232
312,17	316,68	4,51	314,43	»	426,652	94,601	14,789	4,232
				$x_2=0,007$				
278,60	283,16	4,56	280,88	2400	432,353	94,814	14,546	4,265
283,16	287,73	4,57	285,45	»	431,839	94,494	14,581	4,246
309,44	313,97	4,53	311,71	»	429,950	94,912	14,783	4,257
313,98	318,49	4,51	316,24	»	427,741	94,843	14,818	4,252
318,50	320,75	2,25	319,63	1200	214,100	95.156	14,844	4,267
				$x_2=0,008$				
277,46	282,06	4,6	279,76	2400	432,495	94,021	14,523	4,244
291,51	296,09	4,58	293,80	»	430,407	93,975	14,630	4,236
296,09	300,67	4,58	298,38	»	430,136	93,916	14,665	4,231
306,70	311,24	4,54	308,97	»	426,850	94,020	14,746	4,232
311,25	315,79	4,54	313,52	»	426,913	94,034	14,781	4,231
315,79	320,33	4,54	318,06	»	429,794	94,668	14,816	4,263
				$x_2=0,01$				
277,44	282,03	4,59	279,74	2400	431,061	93,913	14,528	4,246
282,03	286,61	4,58	284,32	»	431,064	94,119	14,562	4,256
295,18	302,04	6,86	298,61	3600	644,583	93,963	14,672	4,241
302,04	306,61	4,57	304,33	2400	429,085	93,892	14,715	4,235
303,52	308,08	4,56	305,80	»	428,409	93,949	14,727	4,238
308,08	312,63	4,55	310,36	»	427,966	94,059	14,762	4,242
312,64	317,19	4,55	314,92	»	428,146	94,098	14,797	4,242
				Water–methyl isobutyl ketone				
				$x_2=0,001$				
279,05	283,54	4,94	281,30	2400	429,959	95,759	14,548	4,188
283,54	288,04	4,50	285,79	»	430,481	95,662	14,583	4,181
298,65	303,11	4,46	300,88	»	426,623	95,655	14,699	4,175
309,01	313,47	4,46	311,24	»	426,000	95,516	14,778	4,164
313,47	317,97	4,50	315,72	»	429,723	95,494	14,811	4,161
317,97	322,44	4,47	320,21	»	427,692	95,681	14,847	4,169
				$x_2=0,003$				
277,24	281,82	4,58	279,53	2400	432,784	94,494	14,517	4,255
286,41	290,99	4,58	288,70	»	431,487	94,211	14,588	4,236
308,20	312,74	4,54	310,47	»	427,991	94,271	14,755	4,231
312,75	317,29	4,54	315,02	»	427,948	94,262	14,789	4,228
317,29	321,82	4,53	319,56	»	427,467	94,364	14,825	4,232

TABLE 1 (Continued)

T_1, °K	T_2, °K	ΔT, °K	T_m, °K	τ, sec	Q, J	mc, J/°K	$m_c c_c$, J/°K	C_{sp}, J/g·°K
x_2=0,005								
277,04	281,59	4,55	279,32	2400	431,847	94,911	14,511	4,231
296,52	301,05	4,53	298,79	»	430,646	95,065	14,666	4,231
301,06	305,58	4,52	303,32	»	429,742	95,076	14,701	4,230
310,11	314,62	4,51	312,37	»	429,008	95,124	14,771	4,229
314,63	319,13	4,50	316,88	2400	428,502	95,223	14,805	4,232
x_2=0,006								
278,58	283,05	4,47	280,82	2400	425,327	95,152	14,543	4,235
283,07	287,50	4,43	285,29	»	421,804	95,215	14,578	4,237
287,51	290,88	3,37	289,20	1800	320,034	94,966	14,608	4,222
308,78	313,24	4,46	311,01	2400	423,842	95,032	14,775	4,217
313,26	317,72	4,46	315,49	»	423,861	95,036	14,810	4,215
317,74	322,19	4,45	319,97	2400	423,576	95,186	14,844	4,221
x_2=0,007								
278,60	283,16	4,56	280,88	2400	432,353	94,814	14,546	4,265
283,16	287,73	4,57	285,45	2400	431,839	94,494	14,581	4,246
309,45	313,97	4,52	311,71	2400	429,950	95,122	14,783	4,269
313,98	318,49	4,51	316,24	»	427,741	94,843	14,818	4,252
318,50	320,75	2,25	319,63	1200	214,100	95,156	14,844	4,267
x_2=0,008								
279,90	284,46	4,56	282,18	2400	431,523	94,632	14,537	4,241
284,46	289,00	4,54	286,73	»	429,937	94,700	14,571	4,243
289,01	292,42	3,41	290,72	1800	322,727	94,641	14,602	4,238
292,02	296,52	4,50	294,27	2400	425,719	94,604	14,630	4,235
305,41	309,91	4,50	307,66	»	426,115	94,692	14,733	4,234
309,92	314,40	4,48	312,16	»	425,399	94,955	14,767	4,246
314,41	318,90	1,49	316,16	»	425,582	94,784	14,802	4,235
x_2=0,01								
277,29	281,95	4,66	279,62	2400	436,842	93,743	14,522	4,203
281.96	286,61	4,65	284,29	»	434,791	93,503	14,555	4,188
286,62	291.29	4,67	288,96	»	435,842	93,328	14,591	4,177
291,30	295,96	4,66	293,63	»	435,857	93,532	14,627	4,186
292.61	297,27	4,66	294,94	»	435,424	93,439	14,637	4,180
297,29	301,95	4,66	299,62	»	434,930	93,333	14,673	4,173
301,97	306,63	4,66	304,30	»	434,102	93,155	14,727	4,161
311,32	315,96	4,64	313,64	»	433,252	93,373	14,780	4,169

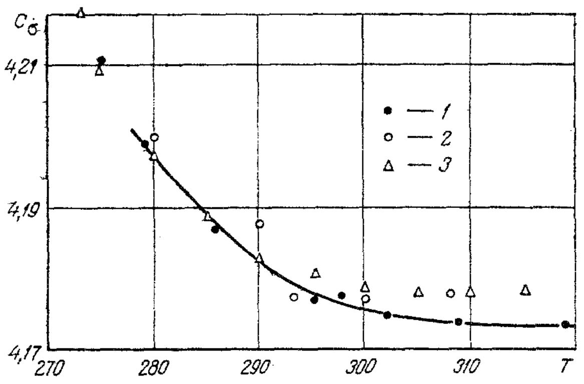

Fig. 1. Specific heat c_σ (J/g•°K) of pure water versus temperature T, °K: 1) experimental data of present study; 2) data of [8]; 3) data of [9].

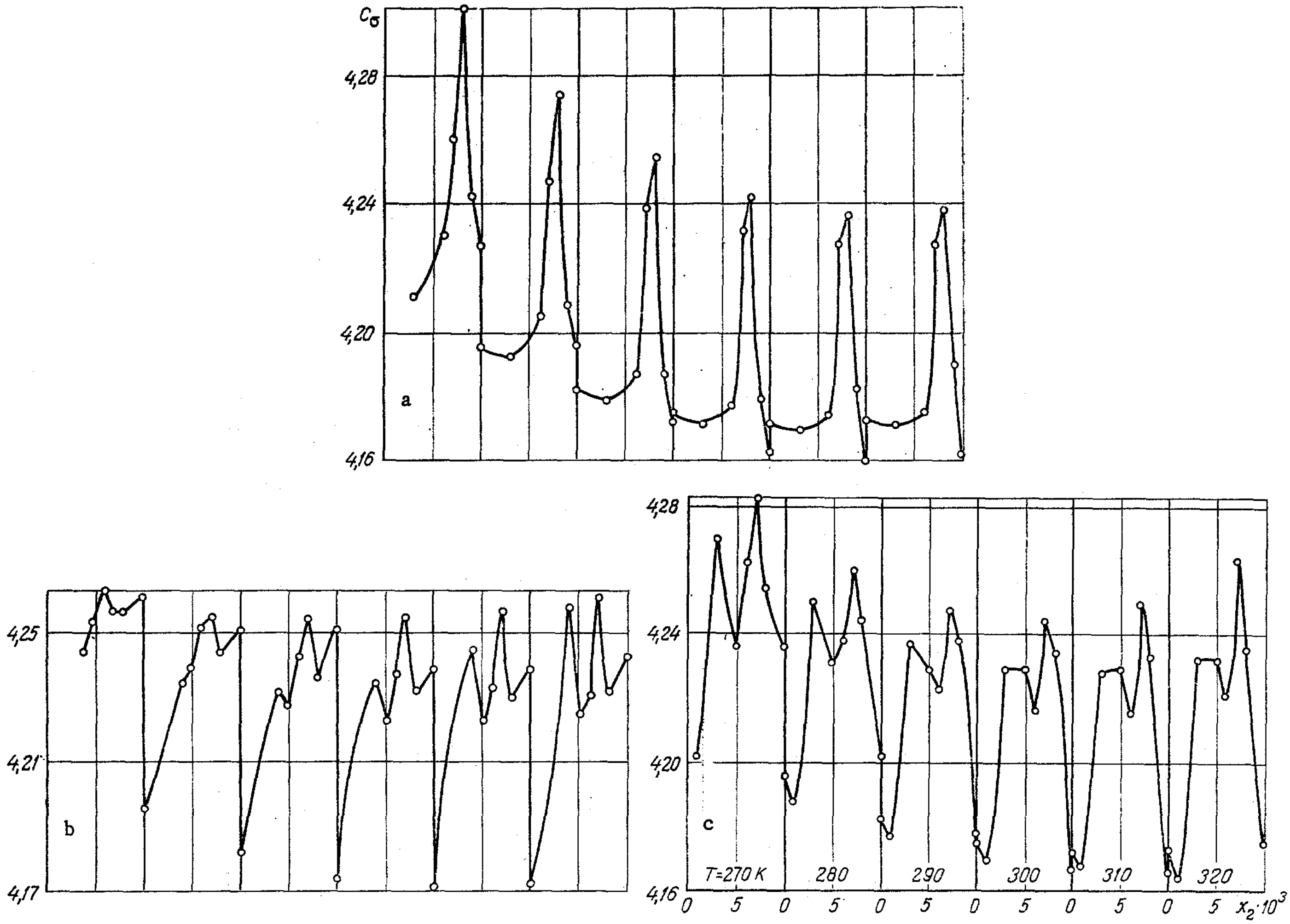

Fig. 2. Isotherms of concentration dependence of the specific heats of the solutions: a) water—methyl ethyl ketone; b) water—methyl butyl ketone; c) water—methyl isobutyl ketone.

solutions studied were prepared from doubly distilled water and analytical-grade ketones. Experimental data on the temperature dependence of the heat capacities of the solutions are presented in Table 1.

Smoothed values of the temperature dependences were used to construct curves of the concentration dependence of the specific heats of the solutions. Isotherms of the concentration dependence of the specific-heats of the solutions are shown in Fig. 2.

Figure 1 shows the temperature dependence of the specific heat of pure water. The presence of a minimum in this curve is maintained in all the aqueous solutions. The minimum is located near a temperature of 310°K (37°C), which corresponds to the normal temperature of a living cell — a fact which deserves special consideration.

The concentration dependences of heat capacity are of a more complex character. For the water—methyl ethyl ketone (C_4H_8O) solution, this function has a maximum at the 0.008 mole % level. The value of this maximum decreases with increase in temperature from 270 to 310°K, and then increases slowly (Fig. 2a).

In the isotherms of the concentration dependence of heat capacities of the water—methyl butyl ketone ($C_6H_{12}O$) and water—methyl isobutyl ketone ($C_6H_{12}O$) solutions there are two maxima of comparable value at concentrations of about 0.003 and 0.007 mole % (Fig. 2b, c).

It is evident from the figures that increase in the number of CH_2 groups as well as the position of these groups in isomer molecules affects the character of the concentration dependence of heat capacity. A detailed evaluation of the results obtained will be presented in a special report. Studies will also be continued. But it remains indisputable that the presence of a second component in an aqueous solution has a significant effect on the water structure, as reflected in the behavior of heat capacity.

NOTATION

c_σ, specific heat of liquid in equilibrium with its saturated vapor; m, mass; T, temperature; ΔT, temperature difference; T_m, mean temperature; τ, time; Q, amount of heat; c_{sp}, specific heat; m_c, mass of calorimeter; c_c, heat capacity of calorimeter.

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EXPERIMENTAL STUDY OF HIGH-TEMPERATURE LIQUID EVAPORATION FROM CAPILLARIES

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UDC 66.047

Experimental studies of liquid evaporation rates from capillaries in air at atmospheric pressure and temperatures near and above the boiling point are compared with the previously developed theory.

It is well known that an increase in the total pressure of a vapor–gas mixture within porous bodies may be a cause of their destruction [1].

To explain this increase in internal pressure with evaporation from capillaries a theory based on consideration of vapor and gas transfer with account taken of gas-kinetic slip [3] was developed [2]. Analysis of these solutions reveals that with a decrease in capillary radius r, the total pressure of the vapor–gas mixture above the meniscus P_e increases, exceeding both the saturated vapor pressure above the meniscus p_s and the pressure P_0 of the gas in the surrounding medium. Physically, this effect is explained by the fact that with decrease in r, hydrodynamic resistance increases, as a consequence of which ever-higher gradients in the total pressure of the vapor–gas mixture are necessary for compensation of the r-independent gas-diffusion counterflow. The solution obtained for small r has the form

$$M = \frac{P_0 D_0}{RTx} \ln \frac{(P_0 - p_{01}) P_e}{(P_e - p_s) P_0}. \quad (1)$$

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