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Volume Characteristics of Lithium Salts in Alcohols

O. V. Eliseeva, E. V. Korotkova, and V. V. Golubev

Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia

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Abstract—The densities of lithium chloride and nitrate in aliphatic alcohols (methanol, ethanol, 1- and 2-propanol, 1- and 2-butanol, and 1- and 2-pentanol) at 298.15 K in the salt concentration range from 0 to 3.5 mol kg^{-1} were measured by means of vibrational densimeter. The resulting density data were used to calculate the apparent and partial molar volumes of the solvents and solutes.

Structural changes in solutions are topical problems of physical chemistry. In dilute solutions, these processes are treated in terms of the Debye–Huckel law. Much more problems arise when one deals with medium or high concentrations of electrolytes in nonaqueous solvents. Because of experimental difficulties, scarce evidence is available for such solutions.

To reveal the effect of anions on processes responsible for structural changes in solutions, we studied volume properties of the title systems. Unfortunately, density data for solutions of lithium salts of a wide concentration range (from zero to saturation) are almost lacking. We can mention only a few works on this subject [1, 2]. Therefore, in the present work we measured the densities of solutions of lithium nitrate and chloride in aliphatic alcohols (methanol, ethanol, 2-propanols, 1- and 2-butanols, and 1- and 2-pentanols) at 298.15 K at salt concentrations ring from 0 to 3 mol kg^{-}. Experimental densities, as well as calculated apparent and partial molar volumes are given in [3, 4] and Figs. 1–5.

For lower errors, partial molar volumes were calculated directly from experimental densities using equations from [5].

$$V_1 = \frac{M_1}{\rho} + \frac{mM_1(1000 + mM_2)}{1000\rho^2} \cdot \frac{\partial\rho}{\partial m}, \qquad (1)$$

$$V_2 = \frac{M_2}{\rho} + \frac{mM_1(1000 + mM_2)}{1000\rho^2} \cdot \frac{\partial\rho}{\partial m}. \qquad (2)$$

Here V_1 and V_2 are the partial molar volume of a solvent and a solute, M_1 and M_2 are the molar weights of the solute and the solvent, m is the molal concentration of the solution, mol kg^{-1}, and ρ is the density of the solution.

The apparent molar volumes (V_Φ) of solutes were calculated by a known equation (3).

$$V_\Phi = \frac{1000(\rho_0 - \rho)}{m\rho\rho_0} + \frac{M_2}{\rho}. \qquad (3)$$

Here ρ_0 is the density of the straight solvent.

The straight solvents are associated liquids involving different associates: chain, cyclic, etc. First salt additions induce profound structural rearrangements, involving all types of interactions: solvent–solvent, solvent–solute, and solute–solute, i.e. ionic association, solute solvation, and solvent–solvent association undergo equal changes. With further increase in elec-

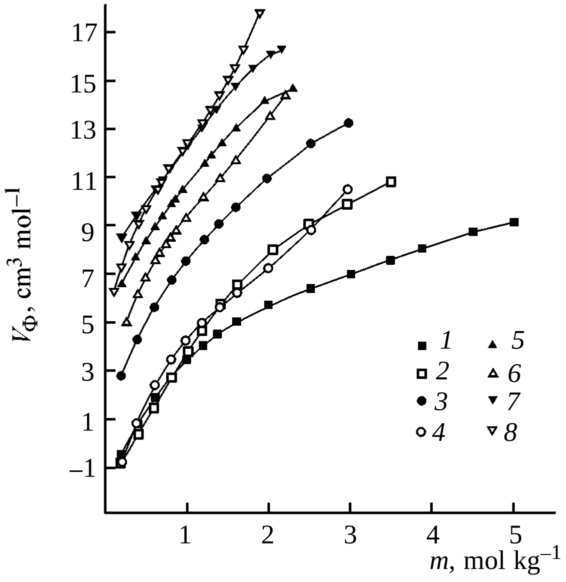

Fig. 1. Dependence of the apparent molar volumes of lithium chloride in aliphatic alcohols on the molal concentrations of solutions at 298.15 K. Solvent: (*1*) MeOH, (*2*) EtOH, (*3*) PrOH, (*4*) 2-PrOH, (*5*) BuOH, (*6*) 2-BuOH, (*7*) 1-C_5H_{11}OH, and (*8*) 2-C_5H_{11}OH.

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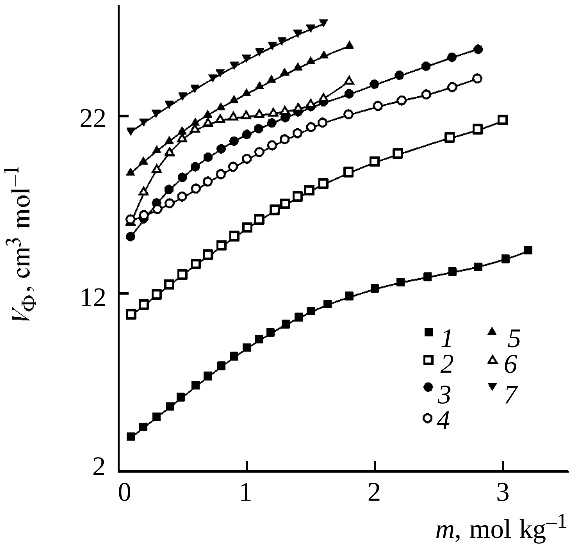

Fig. 2. Dependence of the apparent molar volumes of lithium nitrate in aliphatic alcohols on the molal concentrations of solutions at 298.15 K. Solvent: (*1*) MeOH, (*2*) EtOH, (*3*) PrOH, (*4*) 2-PrOH, (*5*) BuOH, (*6*) 2-BuOH, and (*7*) $C_5H_{11}OH$.

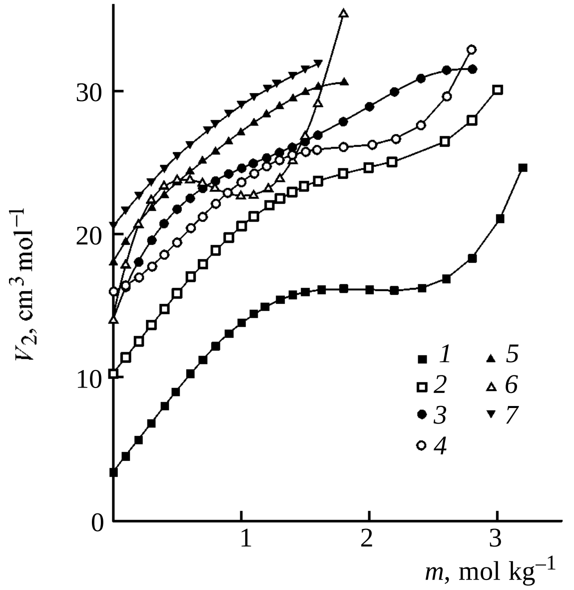

Fig. 4. Dependence of the partial molar volumes of lithium nitrate on the molal concentrations of solutions at 298.15 K. Solvent: (*1*) MeOH, (*2*) EtOH, (*3*) PrOH, (*4*) 2-PrOH, (*5*) BuOH, (*6*) 2-BuOH, and (*7*) $C_5H_{11}OH$.

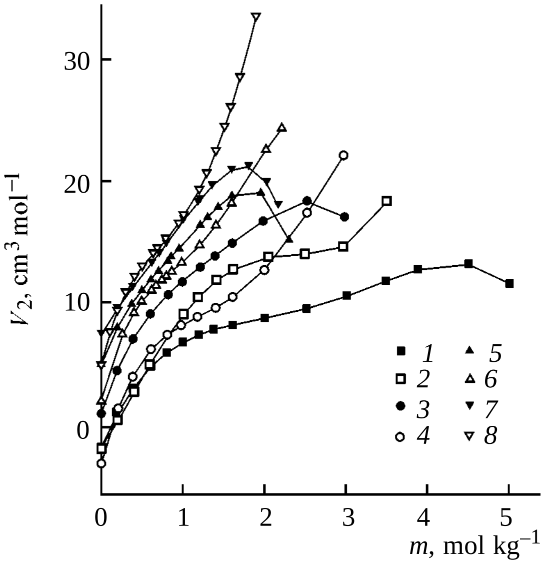

Fig. 3. Dependence of the partial molar volumes of lithium chloride on the molal concentrations of solutions at 298.15 K. Solvent: (*1*) MeOH, (*2*) EtOH, (*3*) PrOH, (*4*) 2-PrOH, (*5*) BuOH, (*6*) 2-BuOH, (*7*) $C_5H_{11}OH$, and (*8*) 2-$C_5H_{11}OH$.

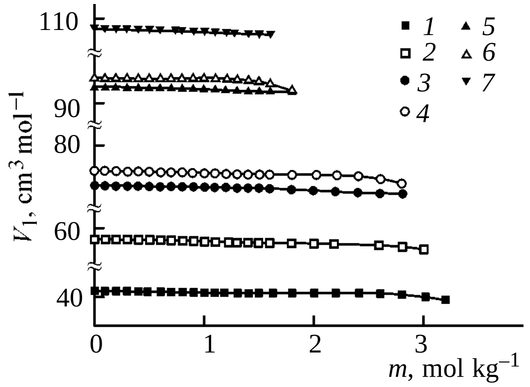

Fig. 5. Dependence of the partial molar volumes of aliphatic alcohols in systems involving lithium nitrate on the molal concentrations of solutions at 298.15 K. Solvent: (*1*) MeOH, (*2*) EtOH, (*3*) PrOH, (*4*) 2-PrOH, (*5*) BuOH, (*6*) 2-BuOH, and (*7*) $C_5H_{11}OH$.

trolyte concentration, the relative contributions of the interactions change in favor of solvation factors.

As seen from Figs. 1–4, with increasing solution concentrations, both the apparent and partial molar volumes of solutes increase. The dependences can be divided into two portions: first 0–1 mol kg^{-1} and second >1 mol kg^{-1}. It is shown in [6] that structure formation under the action of electrostatic forces is almost completed at a concentration of about 1 mol kg^{-1}. At concentrations higher than 1 mol kg^{-1}, packing processes form a “pseudocrystal” structure (such structures are characteristic of solid crystals), and all apparent volume–concentration curves tend to

Experimental slopes (S_V, A_V) of concentration dependences of apparent molar volumes, calculated by different equations

Solvent	LiCl				$LiNO_3$			
	Masson–Randall–Rossini equation [5]		Debye–Hückel equation [5]		Masson–Randall–Rossini equation [5]		Debye–Hückel equation [5]	
	$V_{\Phi0}$	S_V	$V_{\Phi0}$	A_V	$V_{\Phi0}$	S_V	$V_{\Phi0}$	A_V
MeOH	–2.42	6.15	–6.33	23.8	–3.64	12.44	–2.32	14.7
EtOH	–6.03	10.73	–10.22	32.84	5.70	10.88	–0.43	49.75
PrOH	–1.65	10.05	–6.52	38.78	12.63	9.07	9.23	32.44
2-PrOH	–4.42	10.02	–3.36	12.96	12.28	7.94	13.64	6.21
BuOH	2.93	8.82	0.61	38.33	14.66	9.66	9.08	52.03
2-BuOH	0.24	10.47	–4.82	48.52	16.63	6.03	11.09	44.65
C_5H_{11}tOH	3.94	9.45	5.55	11.14	18.35	7.79	19.50	4.28
2-C_5H_{11}OH	5.11	7.2	7.41	3.84				

the molar volumes of solid salts (V_{LiNO_3} 29.22 cm^3 and V_{LiCl} 20.48 cm^3).

All molar volume–concentration curves (V_Φ, V_2) for isoalkyl alcohols pass below than those for the corresponding normal alkyl alcohols, and certain curves have inflection points (Figs. 1–4). It can be proposed that isoalkyl alcohols, having higher dipole moments than primary ones, undergo more intricate association processes. Thus, not only radical chain length, but also isomerism affect structural changes in solutions.

Both apparent and partial molar volumes in systems involving lithium chloride are higher than in systems involving lithium nitrate. However, the curves in methanol, ethanol, and 2-propanol merge up to a concentration of about 1 mol kg^{-1}, and individual properties of each solvent reveal themselves only above that concentration. It should be noted that the concentration dependences of the partial and apparent molar volumes of ethanol and 2-propanol have similar patterns, which is incharacteristic of lithium nitrate. The fact can be explained in no other way than by an anion effect on structural changes, on account of the more branched structure of the nitrate ion compared with chloride (the latter can be represented by a sphere with the charge in the center), whereas, according to [7], "anion much weaker affects the strength of the alcohol–cation bond than cation the strength of the alcohol–anion bond." But, apparently, the chloride ion forms a strong negative electric field around an alcohol molecule (by analogy with the bromide ion), and the lithium cation forms a stronger bond with this associate than with a separate alcohol molecule.

As follows from Figs. 1 and 2, the concentration dependences of apparent molar volumes for both salts (nitrate and chloride) in all the alcohols studied have positive slopes. But, as seen from the table, the results obtained by the Masson–Randall–Rossini and Debue–Hückel equations [5] allow one to judge about the sign of the slope, but appreciably differ quantitatively. However, the experimental slope for lithium chloride, obtained by the Debye–Hückel equation, nicely fits the theoretical value in [5]. Unfortunately, numerical values of $V_{\Phi0}$ are impossible to discuss, since we performed exptrapolation beginning with c = ~0.1 mol kg^{-1} and set ourselves the task to determine the sign of the slope of the $V_\Phi = f(c)$ dependence.

It is seen from Fig. 4, the concentration dependences of the partial molar volumes in 2-butanol and methanol are anomalous compared with those in other alcohols. The similarity of the former two dependences is inexplicable in terms of dielectric constants and dipole moments {methanol: ε 32.63 and μ 1.70; 2-butanol: ε 17.6 and μ 1.79 [8]}. The molecular geometries of the two solvents, too, differ considerably. The reasons for this observable call for further investigation.

Figure 5 shows the dependences of the partial molar volumes of the solvents for lithium nitrate; the corresponding plots for lithium chloride are fully identical. The plots for isoalkyl alcohols are all below the corresponding plots for normal alkyl alcohols; therewith, the plots have similar shapes, and are arranged at almost equal distances form each other, since the partial molar volumes increase by one and the same value with increasing hydrocarbon chain length (namely, by one CH_2 unit).

EXPERIMENTAL

Lithium nitrate of ultrapure grade and lithium chloride of chemical grade were used. Lithium nitrate was recrystallized from twice distilled water and vacuum-dried at 373 K. Lithium chloride was first calcined at 573 K and then twice distilled from twice distilled water, dried with constant stirring at 423 K, and finally vacuum-dried at 373 K. All aliphatic alcohols of chemical grade were purified by known procedures [9, 10]. The residual water, by Fischer titration, was ±0.003 wt% for alcohols and ±0.01 wt% for salts. All solutions were prepared gravimetrically to within $\pm 5 \times 10^{-5}$ g. The thermostating temperature was 298.15±0.01 K. The densities were measured using vibration densimeter. The design and operation of the densimeter were described in [11]. The density was measured to within $\pm 2 \times 10^{-6}$ g cm^{-3}.

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